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## THE PHYSICAL REVIEW

### THE ISOTOPE EFFECT IN BAND SPECTRA, III. THE SPECTRUM OF COPPER IODIDE AS EXCITED BY ACTIVE NITROGEN

BY ROBERT S. MULLIKEN<sup>1</sup>

#### ABSTRACT

**Excitation of spectra by active nitrogen.**—Band spectra of CuF, CuCl, CuBr, and CuI have been obtained by the action of active nitrogen on the vapors of CuF<sub>2</sub>, CuCl and CuCl<sub>2</sub>, CuBr<sub>2</sub>, and CuI, using the method of Rayleigh and Fowler, as previously applied by them to CuCl. Certain additional heads are present in the red, probably due to CuO formed as a result of slight oxygen impurity in the active nitrogen, and then excited by the latter. The halide bands are unusually sharp. Probably excited N<sub>2</sub> molecules, in "impacts of the second kind," put halide molecules into the various excited electronic states necessary for the emission of visible band spectra. Many impacts, however, result in dissociation of the halide molecule, as the iodine arc line  $\lambda 2062$  and over 80 lines of the copper arc spectrum were identified. The list of copper lines is exactly the same for CuCl as for CuI. Analogous results have been obtained with PbI<sub>2</sub>, HgI<sub>2</sub>, and HgBr<sub>2</sub>. Other reactions of active nitrogen are discussed.

**Emission of electronic band spectra by polar molecules.**—It is suggested that the absence of electronic band spectra for the hydrogen, silver and alkali halides may be associated with the non-occurrence of higher valence compounds of type NaCl<sub>2</sub>, and that the emission of any one of the CuX band spectra follows the transfer of a Cu<sup>+</sup> electron in the polar Cu<sup>+</sup>X<sup>-</sup> molecule from its normal state to one of a group of low lying excited states, whose existence can be correlated with the occurrence of the compounds CuX<sub>2</sub>, such easily excited electrons being absent in ions such as Na<sup>+</sup>. The above relation may be accounted for by supposing that polar molecules cannot carry electronic energy in excess of their heat of dissociation into atoms. By analogy with the observed absence of electronic band spectra for compounds of the NaCl type, the band spectra of the alkaline earth halides should not be due to compounds MeX<sub>2</sub>, since the Me<sup>++</sup> ion contains no easily excited electron. The real emitter is probably MeX, which must contain a loosely bound valence electron like that in Me<sup>+</sup> or in Na.

**Analysis of band spectrum of CuI, and confirmation of vibrational isotope effect.**—The CuI bands, excited by active nitrogen, were photographed under moderate dispersion (see Plate I). The wave-lengths of over 260 heads between  $\lambda 5650$  and  $\lambda 3890$  were measured (Tables I-V). No other CuI bands are present between  $\lambda 1900$  and  $\lambda 7000$ . Each Cu<sup>63</sup>I band is found to be accompanied,

<sup>1</sup> National Research Fellow.



wherever resolution and intensity are sufficient, by a weaker  $\text{Cu}^{65}\text{I}$  band, as expected. The  $\text{Cu}^{63}\text{I}$  bands can all be arranged in *five systems*, the vibrational isotope effect serving as an almost indispensable key to this analysis. One system lies in the green; the other four, with their bands closely intermingled, lie in the blue and violet. Equations are given representing the positions of all the  $\text{Cu}^{63}\text{I}$  heads within experimental error, in terms of the initial and final vibrational quantum numbers and their squares. From these equations, the corresponding theoretical equations for  $\text{Cu}^{65}\text{I}$  are calculated. The observed  $\text{Cu}^{65}\text{I}$  heads fall consistently within experimental error in the calculated positions. Near-equality of the coefficients (of both linear and quadratic terms) concerned with the final state of the molecule, shows that the five systems all correspond to a common final electronic state. This is almost certainly the normal state of the  $\text{CuI}$  molecule. Analogous relations probably hold for  $\text{CuCl}$  and  $\text{CuBr}$ , although the analysis is not yet completed. In all cases the vibration frequency is less and the interatomic distance greater for the excited states than for the normal state. The five excited states of the  $\text{CuI}$  molecule correspond to electronic energies equivalent to 2.44, 2.68, 2.70, 2.83, and 2.96 volts. An *energy-level diagram* for  $\text{CuI}$  is given, showing all the electronic and vibrational energy levels, and the observed transitions with their intensities. It is shown that the initial distribution of  $\text{CuI}$  molecules with respect to vibrational energy is of a thermal type and probably corresponds to the existing low temperature, thus differing markedly from the high-temperature non-thermal distribution characteristic of such compounds as  $\text{BO}$  and  $\text{CN}$  as excited by active nitrogen. *Intensity distribution in the  $\text{CuI}$  bands.* A marked tendency is noted here, as previously in the case of  $\text{BO}$ , for numerically large values of  $\Delta n$  to be associated with large values of the initial vibrational quantum number  $n'$ . This causes the maximum of intensity in band sequences (a sequence contains bands for all of which  $\Delta n$  has the same value) to shift from the first to higher members of the sequence, as one proceeds to bands at increasing distances from the system-origin. Both the above effect and a preference for positive values of  $\Delta n$  are explained in terms of Lenz's theory.

#### INTRODUCTION

THE band spectra of the chloride, bromide, and iodide of copper are highly characteristic, and that of the chloride in particular has been the object of much study.<sup>2,3,4</sup> These spectra all lie in the visible. They consist of numerous groups of bands, every group and every individual band being shaded toward the red. For the appearance of these bands, reference may be made to Eder and Valenta's excellent reproductions.<sup>3</sup> The bands are easily excited by the addition of either cuprous salts ( $\text{CuCl}$ ,  $\text{CuBr}$ ,  $\text{CuI}$ ) or cupric salts ( $\text{CuCl}_2$ ,  $\text{CuBr}_2$ ) to flames. Cupric salts easily lose their second halogen atom on heating;  $\text{CuI}_2$  is so unstable that it cannot be made even at room temperature. Hence, since the cu-

<sup>2</sup> For a summary of the literature, see Kayser and Kayser-Konen, *Handbuch der Spektroskopie*, vols. V, VII, section on Cu.

<sup>3</sup> J. M. Eder and E. Valenta, *Atlas typischer Spektren*, Vienna, 1911.

<sup>4</sup> The copper halides are also briefly discussed in H. M. Konen's "Das Leuchten der Gasen und Dämpfe," F. Vieweg und Sohn, Braunschweig, 1913, on pp. 212, 234-5 and 275-6.

pric salts give the same spectra as the corresponding cuprous salts, the spectra have been attributed to the latter.<sup>5</sup> This is confirmed by a quantum theory analysis of the spectra (see below) which shows them to be of the type to be expected for diatomic molecules. The spectrum of copper fluoride ( $\text{CuF}_2$ ) differs from those of the other halides in that it is not readily excited, and in that it consists, so far as is known, only of a single group of bands, which, furthermore, are shaded toward the violet.

Since fairly large isotope effects were to be anticipated in these spectra,<sup>6,7,8</sup> the present study of them was undertaken. The predicted "isotope patterns" have been represented in a diagram on p. 133 of a previous article<sup>8</sup> which will be referred to as (I) in the remainder of the present discussion, and have been confirmed in the actual spectra.<sup>7,8</sup> From the atomic weight, 63.57, the two isotopes of copper which Aston has reported,<sup>9</sup>  $\text{Cu}^{63}$  and  $\text{Cu}^{65}$ , should have an abundance ratio of about 5:2. The largest predicted separation between corresponding bands of  $\text{Cu}^{63}\text{X}$  (where X is any halogen) is for  $\text{CuI}$ , whose spectrum, furthermore, is less complicated than those of  $\text{CuBr}$  and  $\text{CuCl}$ , due to the absence of iodine isotopes. Examination of the  $\text{CuI}$  spectrum was therefore first undertaken. The results of an analysis of the green  $\text{CuI}$  bands have already been reported briefly.<sup>7</sup> The remainder of the  $\text{CuI}$  spectrum has now been analyzed, and the complete data and analysis are given below, together with preliminary and general results on  $\text{CuCl}$  and  $\text{CuBr}$ . The latter will be treated more in detail in a later paper.

#### USE OF ACTIVE NITROGEN IN EXCITATION OF COPPER HALIDE SPECTRA

In their classic work on active nitrogen, Rayleigh and Fowler showed<sup>10</sup> that the  $\text{CuCl}$  band spectrum can be excited by the introduction of  $\text{CuCl}$  vapor into the nitrogen afterglow. They reported that the  $\text{CuCl}$  bands are better visible than in the flame, the usual continuous background<sup>11</sup> in the green being absent. They also found more bands than usual at the ultraviolet end, and further noted that the copper

<sup>5</sup> R. Derichsweiler, Dissertation Bonn, 1906; *Zeits. wiss. Phot.* **4**, 401-17 (1906).

<sup>6</sup> R. S. Mulliken, *Nature*, April 5, 1924.

<sup>7</sup> R. S. Mulliken, abstract of paper given at meeting of Amer. Phys. Soc., *Phys. Rev.* **23**, 767 (1924).

<sup>8</sup> R. S. Mulliken, *Phys. Rev.* **25**, 119 (Feb., 1925): The Isotope Effect in Band Spectra, Part I.

<sup>9</sup> F. W. Aston, *Isotopes*, 2nd ed., 1924. Edw. Arnold & Co., London.

<sup>10</sup> R. J. Strutt, *Proc. Roy. Soc.* **85A**, 219 (1911);

R. J. Strutt and A. Fowler, *Proc. Roy. Soc.* **86A**, 105 (1911).

<sup>11</sup> This is observed in the flame spectra of all copper salts. Apparently it is not really continuous but consists (see ref. 3) of numerous closely-spaced bands (oxide bands?).

arc spectrum was developed, more lines being present than in the flame.

On account of the sharpness and clearness of the heads, and also because of interesting possibilities in regard to the mechanism of excitation, the writer has used active nitrogen as a means of exciting the spectra of all the copper halides. It was found that the bromide ( $\text{CuBr}_2$  was used) and especially the iodide, ( $\text{CuI}$ ) are less readily excited than the chloride (either  $\text{CuCl}$  or  $\text{CuCl}_2$ ), more intense heating and longer exposures being required. Also, the iodide band spectrum is largely masked by the presence of even a small amount of chloride impurity. The intensity of the copper line spectrum, relative to that of the band spectrum, appears to increase markedly in going from chloride to iodide. These differences would seem to be correlated with decreasing stability of the molecules in the order chloride-bromide-iodide. The excitation of the fluoride spectrum, by heating  $\text{CuF}_2$  in active nitrogen, was found even more difficult than that of the iodide spectrum, perhaps on account of the involatility of  $\text{CuF}_2$ ; some weak exposures were, however, obtained.

*Oxide bands.* With all three halides, a set of bands, of variable intensity, occurs in the red. These proved, by approximate determination of their wave-lengths and comparison with Eder and Valenta's excellent reproductions,<sup>12</sup> to be the red bands which are ascribed by Eder and Valenta to copper oxide ( $\text{CuO}$ ), and which occur in the flame spectra of all copper salts. The heads of the bands appear for the most part in pairs, all the heads being shaded toward the red. According to the literature, the members of a pair are ordinarily about equally intense, but in the present experiments, the shorter wave-length component was relatively weak. The following list covers the observed heads, the intensities being given in parentheses, for an unusually intense exposure. The wave-lengths were not carefully measured, but Hertenstein's values<sup>13</sup> are given approximately, except for three apparently new heads at the red end for which the (only roughly approximately) wave-lengths are italicized:  $\lambda$ 6046 (1), 6060 (7); 6148 (2), 6163 (8); 6283 (00?), 6296 (2); 6381 (0), 6403 (1), *6435* (3); *6490* (1), *6530* (1), 6547 (2). Only the stronger heads (int. 2 or

<sup>12</sup> Eder and Valenta.<sup>3</sup> Plates V, 2-3, XXI, 9, and XXV, 8, show these bands especially well. In plate XXI, 9, the stronger heads are shown resolved into what is probably a succession of heads, so that each "head" as used above probably means the first head of a compact group. Kayser and Konen<sup>2</sup> consider it rather doubtful whether these and other bands toward shorter wave-lengths are due to the oxide or the metal. Some of the copper bands of large spacing, as well as other supposed metal bands, have recently been shown (see ref. 6) to be due to a hydride. The red bands are not of this type. It is of course still possible that they are due to  $\text{Cu}_2$ .

<sup>13</sup> H. Hertenstein, *Zeits. wiss. Phot.* 11, 69 and 119 (1912).

more) were definitely observed to be shaded toward the red. It may be noted that only the heads from  $\lambda 6046$  to  $6296$  are found in the Bunsen flame, according to Eder and Valenta, while the oxy-gas flame is needed for the following pair. The occurrence of the bands here is presumably due to the excitation of oxide molecules by active nitrogen. A detailed investigation did not seem worth while, but there was evidence that the bands are favored by a small leakage of air into the halide vapor, or the presence of a little oxygen in the nitrogen used. A dark brown or black deposit, presumably copper oxide, formed in small amounts on the walls of the afterglow tube, was formed more rapidly when air was admitted. This product, separated from copper halide by dissolving the latter in sodium thiosulphate solution, was at first suspected of being a nitride. On heating it with NaOH solution, a strong odor of ammonia was in fact obtained in one case when CuBr had been used (in this case the NaOH was added directly to the thiosulphate solution containing the solid in suspension). Since, however, later tests with Nessler's reagent failed to give any indication of ammonia with the product obtained from CuI, and only a slight test with the CuCl product, the formation of nitride in appreciable amounts must be considered very doubtful.—There is no evidence in the present work of a nitride band spectrum.

#### EXPERIMENTAL METHODS AND WAVE-LENGTH DATA

In producing the active nitrogen, the method used was essentially that of Lord Rayleigh.<sup>14</sup> Commercial nitrogen (99.7 per cent pure according to the manufacturers) contained in a cylinder under pressure was passed through successive tubes containing (a) fragments of yellow phosphorus (b) calcium chloride, (c) soda-lime, (d) phosphorus pentoxide.

The product was usually very nearly free from oxygen—the  $\beta$  and  $\gamma$  bands of active nitrogen, which are due to the presence of oxygen, being very weak—and sometimes contained excess phosphorus vapor. Any considerable amount either of oxygen or of phosphorus vapor caused a marked decrease in the intensity of the copper halide bands. In experiments with CuCl where excess phosphorus vapor was present, it was found that the CuCl spectrum was restored to its original brilliancy by the admission of a small amount of air, sufficient to destroy the phosphorus. The effect was the same whether this was added before or after the activation of the nitrogen, and the amount required had no visible effect on the color or intensity of the afterglow itself.<sup>15</sup>

<sup>14</sup> R. J. Strutt, Proc. Roy. Soc. 85A, 219 (1911).

<sup>15</sup> The effect of adding oxygen here was evidently of an entirely different nature from that in the case of BO (R. S. Mulliken, Nature, Sept. 6, 1924), where no excess of phosphorus was present.

## DESCRIPTION OF PLATE I

Plate I shows most of the CuI bands; *top*, A bands; *middle*, B, C, most of D, and part of E bands; *bottom*, one D band and part of E bands (there are probably a few more, not shown, toward the ultraviolet). Each Cu<sup>63</sup>I head is marked with a vertical line. Each horizontal line serves to connect the members of a band-sequence, i.e. a set of bands having a common value of  $(n''-n')$ ,  $n''$  and  $n'$  being the final and initial vibrational quantum numbers. For each system, the first head  $(n', n'') = (0, 0)$  of the (0) sequence is marked by a *very* heavy vertical line, accompanied by the letter (A, B, etc.) which has been assigned to the system. With this as an origin, the numbering of the other sequences and of the individual bands can be found very readily from the reproduction. Thus, in the A system, the (0) sequence, from left to right, contains the bands (0,0), (1,1), (2,2), (3,3), . . . The next sequence (+1) on the right, contains the bands (0,1), (1,2), (2,3), (3,4), (4,5), . . . On the left of the origin is the (-1) sequence, with bands (1,0), (2,1), (3,2), (4,3), (5,4), . . . ; with the (5,4) head, this sequence slightly overlaps the (0) sequence. It will be noted that on each side of the origin the spacing of the first heads of successive sequences is approximately constant, but that it differs markedly for the positive and negative sequences. This is because these first heads are (0,0), (1,0), (2,0), (3,0), . . . for the negative, and (0,1), (0,2), (0,3), . . . for the positive sequences. For the former the spacing is determined by the *initial*, for the latter by the *final*, vibration frequency of the molecule. To avoid confusion, alternate sequences have been marked in the A bands by verticals of different height; while in the B, C, D, and E bands, which are badly mixed together in the middle of the spectrum, a vertical of characteristic height (diminishing in the order named) is used for each.

The A bands in particular show a typical intensity distribution. As can be seen in the reproduction, the sequences near the origin are the most intense, with some preference for the positive sequences. In the low-numbered sequences, the first head is the most intense, but the intensity maximum shifts to the second head with the sequences  $\pm 3$ , and to higher-numbered heads for the higher sequences.

For each Cu<sup>63</sup>I head, there is a corresponding weaker Cu<sup>65</sup>I head *nearer the origin* in each case. These begin to be resolved at about the sequences  $\pm 2$ . In the reproduction, resolution is apparent in the A system at +3, in the other systems (except B, which is too faint) at +2. In the negative sequences, the Cu<sup>65</sup>I heads are not visible, except rather vaguely in the A sequences -3 and -4. This is due partly to low intensity, partly to concealment by the shading of corresponding Cu<sup>63</sup>I heads. Examination of the manner in which, in the positive sequences, the separation between the heads of the two isotopes converges toward zero as the origin is approached, will show the value of the isotope effect as a means of locating the latter. (Casual inspection of the reproduction would probably lead to a false assignment, due to the different intensities of the heads of the two isotopes; the (+1) sequence would probably be called (0). Careful inspection of the original negative, however, and especially measurement gives the correct assignment without difficulty.)

## BANDS OF COPPER IODIDE

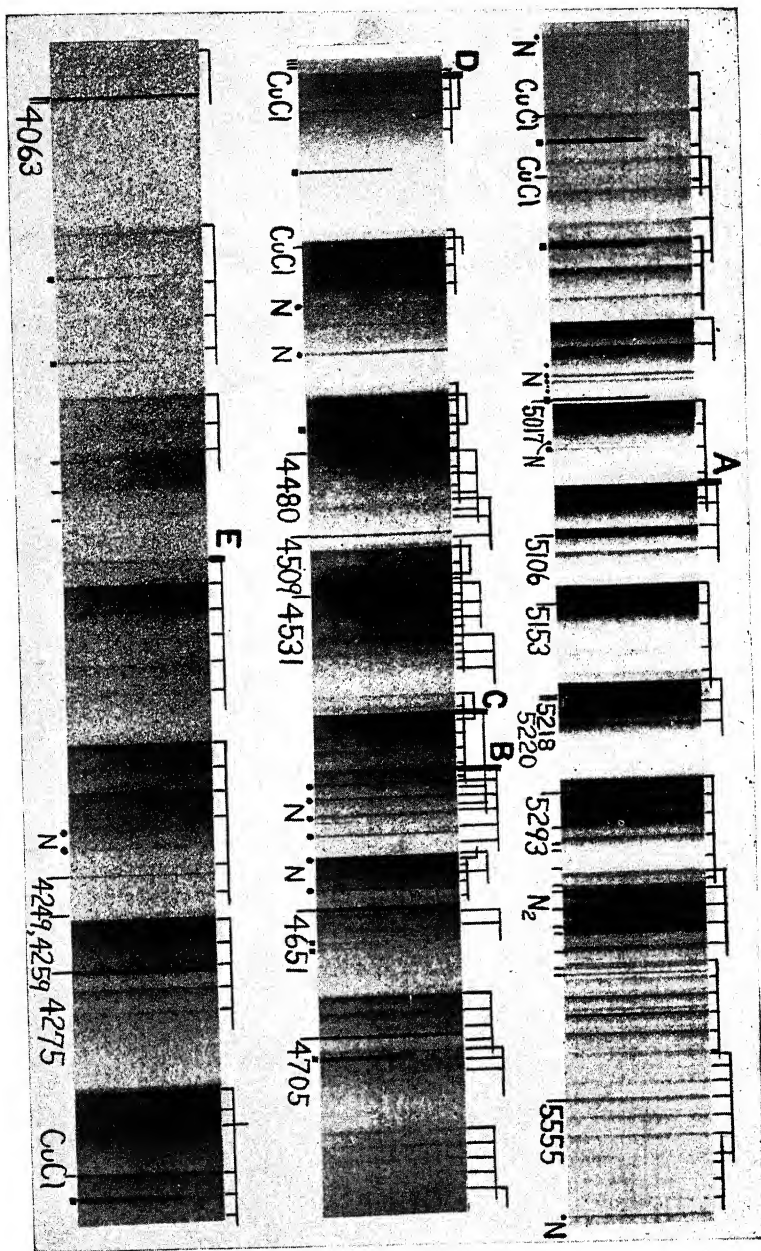


Plate I. Spectrograms showing most of the CuI bands.





The discharge tube for activating the nitrogen, and the attached afterglow tube, were of Pyrex glass of about 8 mm internal diameter. The arrangement is shown in Fig. 1. The discharge was maintained between two tungsten electrodes which were about 10 cm apart. A type E Clapp-Eastham transformer was used at maximum amperage on a 110 volt circuit, with a spark-gap and two large Leyden jars in parallel in the secondary circuit. The activated nitrogen was pumped rapidly out, through a black-painted light trap *T*, into the afterglow tube. The latter was attached at right angles to the discharge tube. The copper salt was contained in a small bulb *B* connected to the afterglow tube at a point just below the point of entrance of the active nitrogen. The bulb was heated by a Bunsen flame just short of its softening point. The quartz

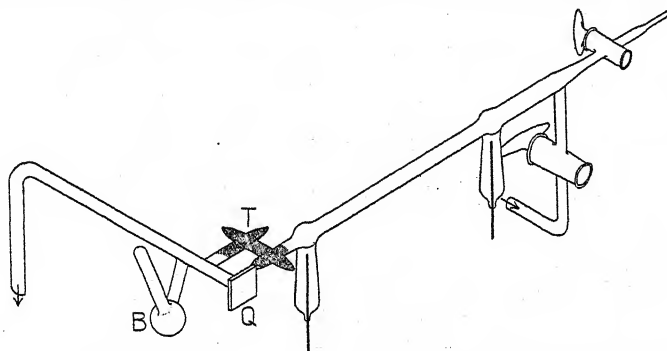


Fig. 1. Arrangement of discharge and afterglow tube for exciting spectra by means of active nitrogen.

window *Q*, fastened with DeKhotinsky cement, was kept cool by means of a ring of wet filter paper on the adjacent section of the afterglow tube. The discharge tube terminal nearer the afterglow tube was earthed, to prevent stray discharge through the latter. In early experiments, where this precaution was not taken, nitrogen lines were present in the spectrum; they were absent from the later photographs, although nothing else was changed. A nitrogen flow rate of 20-60 liters (at 1 atmosphere pressure) per hour was used, with a pressure of about 15-40 mm in the afterglow tube.

The spectra were photographed with a Hilger glass constant-deviation prism spectrograph. The dispersion ranged from about 12 Å/mm at  $\lambda 4000$  to 36 Å/mm at  $\lambda 5000$  and 72 Å/mm at  $\lambda 6000$ . Panchromatic, special green-sensitive, and contrast plates were used for best results with the red, green, and blue to violet regions, respectively. The ultra-violet was examined with quartz spectrographs.

As wave-length standards for the bands, the interspersed Cu lines were used, supplemented by helium lines (plus  $H\beta$ ,  $H\gamma$ , and  $H\alpha$ ) from a super-



posed comparison spectrum, and in the yellow-green, where Cu lines were scarce, by certain  $N_2$  band-heads of the first positive group ( $\alpha$  bands of the afterglow); the latter are very sharp and appear to have been measured accurately to 0.01A. In one photograph N lines resulting from stray discharge (see above) were also available.

In the case of CuI, the exposure used for measurement was one of about three hours duration on a special green-sensitive plate. Enlargements from this are shown in Plate I. The type of plate used is fine-grained, and so, with good focus and a narrow slit, permitted unusually good resolution for the size of the instrument. Practically every distinct head on the plate, including very weak ones, was carefully measured. The results are given in Tables I-V. It can be stated definitely that there are no additional bands of appreciable intensity, at least in the region  $\lambda 1900$ -7000. The precision of the measurements can be gauged by the magnitude of the values in the Obs.-Calc. (O-C) columns. A slight constant error is

TABLE I

*A bands*

Note for Tables I-V: The vibrational quantum numbers are given under  $n'$  and  $n''$ . The "calculated" wave-numbers used for computing the values under "O-C" (observed minus calculated) for  $Cu^{63}I$  and in obtaining the calculated isotopic displacements, were obtained from the equations of Table 6. Isotopic displacements, i.e.  $\nu(Cu^{65}I) - \nu(Cu^{63}I)$ , are given in wave-number units. Wave-numbers in brackets are calculated values, inserted where measurements were not obtained. Nitrogen lines (due to stray discharge, see above), of which a small number were present, and which in some cases (marked "also N line") were superposed on CuI heads, could be picked out by the fact that they extended beyond the CuI heads at the edges of the exposure.

$n'$	$n''$	$Cu^{63}I$ heads				$Cu^{65}I$ heads			Isotopic displacement	
		Int.	$\lambda(I.A.)$	Wave-no.	O-C	Int.	$\lambda(I.A.)$	Wave-no.	Obs.	Calc.
8	3	0	4886.0	20461	-10	0-*	4887.6	20454	-7	-6.7
4	0	0	72.77	516.5	-2	0*	74.69	508.4	-8.1	-8.0
5	1	0+	89.57	446.0	0	0+*	91.15	439.4	-6.6	-7.1
6	2	0	4917.93	369.5	-1	0*	4909.40	363.4	-6.1	-6.2
7	3	00	28.4	285	-7	00*	29.6	280	-5	-5.2
3	0	1	19.09	323.3	1	1*	20.86	316.0	-7.3	-6.1
4	1	1	35.59	255.4	1	1-*	36.73	250.7	-4.7	-5.4
5	2	0	53.16	183.5	0	0*	54.19	179.3	-4.2	-4.5
6	3	00		[ 109.3 ]						
7	4	00		[ 031.9 ]						
2	0	3	68.33	121.9	0		69.24	118.2	-3.7	-4.2
3	1	2	83.88	059.1	0		84.85	055.2	-3.9	-3.5
4	2	0		[19992.2]						
5	3	00		[ 920.4 ]						

\* The high apparent intensities of the  $Cu^{65}I$  heads in this region are due to their superposition on the shading from corresponding  $Cu^{63}I$  heads.

TABLE I—continued

$n' n''$	Cu <sup>63</sup> I heads				Cu <sup>65</sup> I heads			Isotopic displacement	
	Int.	$\lambda$ (I.A.)	Wave-no.	O—C	Int.	$\lambda$ (I.A.)	Wave-no.	Obs.	Calc.
1 0	5	5019.74	915.8	-1				-2.1	
2 1	1	34.61	857.0	-1				-1.6	
3 2	000		[ 796.3]					-0.9	
4 3	0	66.65	731.4	0				-0.2	
5 4	0+	84.52	662.1	-1				0.6	
6 5	00		[ 591.5]						
0 0	7	72.83	707.4	0				0.0	
1 1	0+	87.16	651.9	-1				0.5	
2 2	1	5101.92	595.0	-1				1.0	
3 3	1	17.31	536.1	1				1.6	
4 4	000		[ 471.5]						
0 1	5	41.12	445.6	2					
1 2	1	55.84	390.1	-1					
2 3	00-	70.75	334.2	-1	000		[19338.7]	3.6	
3 4	0	86.80	274.4	-1	00	5185.95	277.5	3.1	4.2
4 5	0	5202.74	215.3	2	00	5201.18	221.1	5.8	4.9
0 2	5	12.18	180.5	-1	2	10.71	185.9	5.4	5.2
1 3	3	26.08	129.5	0	1	24.28	136.1	6.6	5.7
2 4	1	41.03	074.9	0	0	39.25	081.4	6.5	6.1
0 3	2	83.80	18920.5	0	0	81.80	18927.7	7.2	7.8
1 4	4	97.55	871.4	1	1	95.17	879.9	8.5	8.2
2 5	3	5312.42	818.6	2	1	5310.05	827.0	8.4	8.7
3 6	1	28.53	761.7	1	0	26.09	770.3	8.6	9.2
4 7	00	45.8	701	-1	000	43.8	708	7	9.8
5 8	0	64.09	637.3	-1	0	61.3	647	10	10.5
0 4	1	57.42	660.5	0	0	54.27	671.5	11.0	10.3
1 5	3	71.47	611.7	0	1	68.16	623.2	11.5	10.7
2 6	4	86.50	559.8	0	2	83.22	571.1	11.3	11.1
3 7	3†	5402.18	506.1	1	1	98.74	517.7	11.6	11.6
4 8	1-	18.94	448.7	1	0-	5415.71	459.7	11.0	12.2
0 5	0	33.48	399.3	-3	00	28.03	417.8	18.5	12.9
1 6	0+	46.60	355.0	0	1†	42.41	369.1	(14.1)	13.2
2 7	1	61.30	305.6	1	0	57.45	318.5	12.9	13.6
3 8	2	77.09	252.8	1	1	73.04	266.3	13.5	14.1
4 9	1	94.07	196.4	2	0	89.88	210.3	13.9	14.6
5 10	0	5512.79	134.6	-1	00	5507.72	151.3	16.7	15.3
0 6			[ 145.4]						15.3
1 7	00	24.34	096.7	-3	000	19.1	114	17	15.6
2 8	0	38.88	049.2	-2	00	34.07	064.9	15.7	16.0
3 9	1-	54.02	000.0	1	0	48.16	019.0	19.0	16.5
4 10	0+	71.04	17945.0	1	0-	65.21	17963.8	18.8	17.0
5 11	0	88.76	888.1	3	00	83.29	905.6	17.5	17.6
6 12	00	5608.9	824	0	00	5603.8	840	16	18.3
2 9	000	17.3	797	-1					18.4
3 10	00	32.5	749	1	000	26.8	767	18	18.9
4 11	00	49.7	695	1	000	43.1	716	21	19.4

† Also N<sub>2</sub> head.

Note: Average value of "observed" minus "calculated" isotopic displacement, excluding from the average only (0,5), (1,6), and bands where the Cu<sup>65</sup>I head has an intensity less than 00, is +0.05.

TABLE II

*B bands*

Note: because of the low intensity or absence of bands for which an appreciable separation of the heads of the two isotopes would be expected, no measurements could be made on Cu<sup>65</sup>I heads. Indications of the (0,2) head of Cu<sup>65</sup>I were seen, however.

<i>n' n''</i>	Cu <sup>63</sup> I heads					Remarks
	Int.	$\lambda$ (I.A.)	Wave-no.	O-C		
2 0	0-	4498.26	22224.6	0		
3 1	00	4504.79	192.4	0		
4 2	00	11.19	160.9	2		Also 1, 8 E (Cu <sup>65</sup> I)
1 0	1-	46.77	21987.5	-1		
2 1	0	52.63	959.2	-1		
3 2	00	58.11	932.8	3		
4 3			[ 897.9]			
0 0	1d	96.95	747.5	-1		Also (weak) 3,3C
1 1	1	4601.58	725.6	2		Also (strong) N line
2 2	1	07.07	699.7	2		Also (strong) N line
3 3	00	13.09	671.4	2		
4 4	00	19.95	639.2	0		
5 5	00	26.60	608.1	0		
6 6			[ 574.3]			
0 1	0+	4653.50	21483.2	-1		
1 2	0-	58.62	459.6	-2		Also 4, 5C?
2 3			[ 437.1]			A group of heads (see foot-
3 4			[ 411.0]			note) present here may in-
4 5			[ 383.1]			clude both B and C heads;
5 6			[ 353.4]			but the data do not agree
						well with either.
0 2	0-	4711.34	219.5	-2		
1 3	00	15.00	203.0	2		Also 4, 6 C?
2 4	00	19.85	181.2	3		
3 5	00d	23.69	164.0	9		Fused with 5, 7 C?
4 6			[ 128.7]			Possibly present but con-
5 7			[ 101.0]			fused by C heads.

Note: wave-numbers of unidentified heads, with intensities: 21342.1(00); 21357.5 (00-); 21370.3 (00); 21386.5 (00); 21402.9 (0-); 21417.7 (00); 21431.2 (0-); 21445.2 (00); 21473.7 (0); 21548.2 (00); 21581.1 (00?); 21657.3 (00); 21691.1 (00); 21710.8 (00); 21739.0 (00?); 21823.0 (00); 21905.7 (00); 22178.0 (00); 22192.4 (00); 22418.4 (00+); 22431.9 (00); 22771.0 (00); 22802.4 (00); 22833.3 (00); 22866.8 (00).

TABLE III

*C bands*

<i>n'</i>	<i>n''</i>	Cu <sup>63</sup> I heads				Cu <sup>65</sup> I heads				Isotopic displacement	
		Int.	$\lambda$ (I.A.)	Wave-no.	O-C	Int.	$\lambda$ (I.A.)	Wave-no.		Obs.	Calc.
3	0	weak or absent, [22534.9]									
4	1	masked by CuCl [ 497.7]									
2	0	00	4482.03	305.1 <sup>1</sup>	-3						
3	1	00?	89.81	266.4	-5						
4	2	00-	96.88	231.4	-4						
5	3	00	4502.41	204.1	4						
6	4			[ 165.3] <sup>2</sup>							
1	0	2-	27.92	079.0	-1						
2	1	0-	35.11	044.0	-1						
3	2	00	41.91	011.0	1						
0	0	2-	75.15	21851.1	0						
1	1			[ 816.9]							
2	2	masked by 5,13 E [ 782.8]									
3	3	masked by 0,0 B [ 749.2]									
4	4	00	4603.31	717.4	1						
5	5	00	10.64	682.9	0						
0	1	3?	30.63	589.3	1						
1	2	0	38.03	554.9	0						
2	3	..		[ 522.2]							
3	4	masked by Cu [ 489.9]									
4	5	0-	58.62	459.6 <sup>3</sup>	2						
5	6			[ 426.4] <sup>4</sup>							
6	7			[ 395.3] <sup>4</sup>							
7	8			[ 364.6] <sup>4</sup>							
8	9			[ 334.3] <sup>4</sup>							
0	2	1+	87.80	326.0	0	0	4686.84	21330.4	4.4	5.4	
1	3	1-	93.97	295.3	1	0-	93.35	300.8	5.5	5.7	
2	4	0-	4701.72	262.9	0	00	4700.21	269.7	6.8	6.0	
3	5	00	08.72	231.3	-1						
4	6	00	14.99	203.0 <sup>5</sup>	2						
5	7	00d	23.69	164.0 <sup>6</sup>	-7						
6	8	00	29.54	137.8 <sup>7</sup>	-3						
7	9	00	35.59	110.8 <sup>7</sup>	-1						
0	3	00	45.96	064.7	-1	00	43.59	075.2	10.5	8.0	
1	4	0+	52.64	035.1	0	00	50.90	042.8	7.7	8.3	
2	5	00+	59.35	005.4	0	00	57.47	013.7	8.3	8.6	
3	6	00-	66.14	20975.5	0	00-	64.37	20983.3	7.8	8.8	
4	7	00	72.81	946.2 <sup>8</sup>	0						
5	8			[ 917.0] <sup>9</sup>							
6	9			[ 888.5]							
0	4	00?	....	[ 806.4]							
1	5	00?	....	[ 777.1]							
2	6	00?	....	[ 748.3]							

<sup>1</sup> Also 6,12 (Cu<sup>65</sup>I).<sup>2</sup> Confused by E and B heads.<sup>3</sup> Also 1,2 B.<sup>4</sup> See remark in Table II on heads in this region.<sup>5</sup> Also 1,3 B.<sup>6</sup> Fused with 3,5 B?<sup>7</sup> Confused by B heads, see Table II.<sup>8</sup> Also 0,3 B.<sup>9</sup> Confused by B.

TABLE IV

*D bands*

<i>n'</i> <i>n''</i>	Cu <sup>63</sup> I heads				Cu <sup>65</sup> I heads			Isotopic displacement	
	Int.	$\lambda$ (I.A.)	Wave-no.	O-C	Int.	$\lambda$ (I.A.)	Wave-no.	Obs.	Calc.
2 0	0-	4281.97	23347.2 <sup>1</sup>	..					
1 0	1	4320.01	141.6	0					
0 0	2+	59.95	22929.6	0					
1 1	1+	69.93	877.3 <sup>2</sup>	-1					
0 1	3	4410.76	666.0	0					
0 2	2	62.22	404.1	0	0+	4461.08	22409.8	5.7	5.4
1 3	1	71.64	356.9 <sup>3</sup>	2					
0 3	1	4514.76	143.4 <sup>4</sup>	0	0	4513.31	150.5	7.1	8.0
1 4	0	24.69	094.8	0	0+	22.46 <sup>5</sup>	105.7	10.9	8.4
0 4	0-d	68.50	21882.9	0	0-	66.31	21893.4	10.5	10.6
1 5	0d	78.15	836.8 <sup>6</sup>	0		masked by 0,0 C			
1 6	00	4632.39	581.1	2					

<sup>1</sup> Doubtful, in shading of 3,5E.<sup>2</sup> Also 2,6 E.<sup>3</sup> Also (weak) 3,9 E (Cu<sup>65</sup>I).<sup>4</sup> Also (weak) 1,8 E.<sup>5</sup> Also 3,10 E (Cu<sup>65</sup>I).<sup>6</sup> Also 3,11 E.

TABLE V

*E bands*<sup>1</sup>

<i>n'</i> <i>n''</i>	Cu <sup>63</sup> I heads				Cu <sup>65</sup> I heads			Isotopic displacement <sup>2</sup>	
	Int.	$\lambda$ (I.A.)	Wave-no.	O-C	Int.	$\lambda$ (I.A.)	Wave-no.	Obs.	Calc.
3 0	0	4054.17	24659.0	0					
4 1	..	....	[ 617.4]	..					
2 0	1	91.32	435.1	0					
3 1	0	....	[ 395.8]						
4 2	0	4105.02	353.6	-2					
5 3	0	12.34	310.2	-5					
6 4	00	18.51	273.8	0					

<sup>1</sup> Besides the heads recorded in the table, some additional weak heads, mostly further toward the ultraviolet, were found in photographs with the quartz spectrograph. These are shaded toward the red, like the other CuI bands. Several attempts were made to obtain these bands in sufficient intensity for good measurements, but this finally appeared to be not worth while. The data below were obtained with a weak exposure and wide slit. The presence of CN and CuCl bands as impurities also increased the difficulties; NO and I<sub>2</sub> bands were not present in this region. They suffice, however, in spite of poor agreement with calculated values, to establish without much doubt that the observed bands are a (not unexpected) continuation of the E bands, and not an independent system. The intensities were for the most part too low for identification of Cu<sup>65</sup>I heads. The measured values are (with calculated values in parentheses): 24526, (int. 00) (6,3 E=24533); 24656, (0) (3,0 E=24659); 24875, (00) (4,0 E=24881); 24983, (00); 25045, (00) (6,1 E=25055); 25079, (00) (5,0 E, Cu<sup>65</sup>I,=25089); 25090, (00) (5,0 E=25100); 25235, (00), superposed on CuCl head (8,2 E=25223); 25265, CuCl head (7,1 E=25271); 25311, (00d) (25318=6,0 E); 25378, (000d); 25493, (00d) (8,1 E=25485); 25533, (000d) (7,0 E=25534); 25647, (000) (9,1 E=25697); and perhaps a few additional weaker heads.

<sup>2</sup> Average value of "observed" minus "calculated" isotopic displacement, excluding heads marked \* or ?, or of intensity less than 0, is -0.4.

TABLE V—continued

$n'$ $n''$	Cu <sup>63</sup> I heads				Cu <sup>65</sup> I heads			Isotopic displacement	
	Int.	$\lambda$ (I.A.)	Wave-no.	O-C	Int.	$\lambda$ (I.A.)	Wave-no.	Obs.	Calc.
1 0	1—	29.38	209.9	0	*0?	4130.32	24204.4 <sup>2</sup>	-5.5	-2.3
2 1	0	35.82	172.2	0	*0—?	36.49	168.3 <sup>3</sup>	-3.9	-2.0
3 2	0	42.22	134.9	1					
0 0	0	68.52	23982.6	0					
1 1	2	74.60	947.6	1					
2 2	1—	80.85	910.9	0					
3 3	00	87.55	873.6	0					
4 4	0+	94.12	836.2	0					
5 5	00	4200.98	797.3	-1					
0 1	2	14.64	720.2	1	0?	.....	.....	.....	2.7
1 2	0	21.03	684.2	-1					
2 3	2—	27.00	650.8	1	0—	4226.39	23654.2	3.4	3.5
3 4	0	33.75	613.1	-1					
4 5	000	.....	[ 578.3]						
5 6	00	47.01	539.4	-2					
6 7	00	53.28	504.7	0					
0 2	3	61.74	458.1	0	1	60.72	463.6	5.5	5.4
1 3	0—	68.14	422.8	-2	....	.....	[ 428.5]	.....	5.7
2 4	00	74.11	390.1	-1	00	72.83	397.1	7.0	6.0
3 5	1—	80.06	357.5	1	0—	79.07	363.4	5.9	6.4
4 6	1—	86.50	322.5	1	00	.....	[ 329.3]	.....	6.8
5 7	000	.....	[ 286.5]						
0 3	2+	4309.62	197.4	0	1—	4308.17	205.2	7.8	8.0
1 4	1	15.42	166.2	1	0	14.06	173.5	7.3	8.3
2 5	.....	masked	[ 133.2]		*	masked	[ 141.8] <sup>4</sup>	.....	8.6
3 6	000	.....	[ 100.3]				[ 109.2]	.....	8.9
4 7	0*	masked	[ 066.8] <sup>5</sup>		00	32.30	076.0	[9.2]	9.3
5 8	0—	40.45	032.6	0	00	39.02	040.2	7.6	9.6
6 9	00	46.80	22999.0	1					
0 4	1*	58.34	938.1 <sup>6</sup>	0	0*	56.19	22949.4 <sup>6</sup>	(11.3)	10.7
1 5	2—	64.05	908.1	0	0+	62.12	918.2	10.1	10.9
2 6	1+*	69.93	877.3 <sup>7</sup>	1	0—	68.00	887.4	10.1	11.2
3 7	0—	76.11	844.9	0	00	74.11	855.4	10.5	11.4
4 8	000	82.27	812.8	0	000	79.95	824.9	12.1	11.7
5 9	00—	88.55	780.2	0	000	86.60	790.3	10.1	12.0
6 10	000	94.86	747.5	0	000	92.77	758.3	10.8	12.4
7 11	000—		[ 713.2]						
0 5	0+	4408.07	679.3	-1	0—	4405.53	692.4	13.1	13.2
1 6	1—	13.75	650.1	-1	*	masked	[ 663.6] <sup>8</sup>	.....	13.5
2 7	1*	19.08	622.8 <sup>9</sup>	1	0+	16.62	635.4	12.6	13.7
3 8	1—	25.07	592.2	1	0—	22.50	605.3	13.1	14.0
4 9	0*	31.25	560.7 <sup>10</sup>	0	00		[ 575.0]		14.3

<sup>3</sup> Intensity doubtful.<sup>4</sup> Masked by 1,0 D.<sup>5</sup> Masked by CuCl.<sup>6</sup> Also CuCl?<sup>7</sup> Also 1,1 D.<sup>8</sup> Masked by 0,1 D.<sup>9</sup> Also 1,2 D.<sup>10</sup> Also N  $\lambda$ 4431.

TABLE V—continued

$n' n''$	Cu <sup>63</sup> I heads			Cu <sup>65</sup> I heads			Isotopic displacement	
	Int.	$\lambda$ (I.A.)	Wave-no. O—C	Int.	$\lambda$ (I.A.)	Wave-no.	Obs.	Calc.
0 6	0	58.40	423.3 -1					
1 7	1	63.60	397.2 1					
2 8	1+	69.24	368.9 1	1d	65.93	385.5	16.6	16.2
3 9	1+	75.05	339.9 1	1*+	71.64	356.9 <sup>11</sup>	17.0	16.4
4 10	1—	masked [	309.6] <sup>12</sup>	0—d	78.01	325.1	.....	16.7
5 11	0—d	86.89	280.9 1	0—	84.42	293.2	12.3	16.9
6 12	00d	93.69	247.2 -2	00	89.81	266.4	19.2	17.2
0 7	.....	masked [	168.9] <sup>12</sup>	00	4506.19	185.5	.....	18.4
1 8	1*+	4514.76 <sup>13</sup>	143.4 1	00*	11.19	160.9 <sup>13</sup>	[17.5]	18.5
2 9	0+	20.62	114.7 -1	0+	16.94	132.7	18.0	18.7
3 10	0+	26.28	087.0 -1	0*+	22.46	105.7 <sup>14</sup>	18.7	18.9
4 11	00	31.88	059.7 0	... masked <sup>15</sup> [	078.6]			19.1
5 12	0	37.65	031.7 1	0—	33.36	052.5	20.8	19.3
6 13	0d	43.71	002.3 0	00	39.07	024.8	22.5	19.5
7 14	00—	49.73	21973.2 1					
8 15	00	55.93	943.3 2					
2 10	00d	72.80	862.3 -2					21.2
3 11	0d*	78.15	836.8 <sup>16</sup> -1	masked by 2,10 of Cu <sup>63</sup> I				21.3
4 12	0d	83.46	811.5 0	masked by 3,11 of Cu <sup>63</sup> I				21.5
5 13	0d*	88.95	785.4 <sup>17</sup> 1	masked by 4,12 of Cu <sup>63</sup> I				21.7
6 14	00d	94.69	758.2 2					21.9
7 15	00	4600.23	732.0 4					
3 12	*	masked [	589.3] <sup>18</sup> -1					
4 13	00	35.80	565.2 1					
5 14	00	41.50	538.7 0					
6 15	0—d	49.24	508.9 -3					

<sup>11</sup> Also 1, 3 D.<sup>12</sup> Masked by Cu.<sup>13</sup> For 4514, also (strong) 0,3 D; for 4511, also 4,2 B.<sup>14</sup> Also (strong) 1,4 D.<sup>15</sup> Masked by 1,0 C.<sup>16</sup> Also 1,5 D.<sup>17</sup> Also 2,2 C.<sup>18</sup> Masked by 0,1 C.

likely, due to the uncertainty as to the proper mode of setting on heads which are shaded off toward one side. The following measured values for a few of the strongest CuCl heads, present as impurities among the CuI heads, may be compared with presumably much more accurate values as determined by Kien<sup>16</sup> under high dispersion:

Present results: 4333.37, 4353.93, 4412.16;

Kien, 4333.254, 4353.892; 4412.14.

Detailed data on the CuBr and CuCl bands will be reserved for a later paper.

#### ANALYSIS OF CuI BANDS

As will be seen from the tables, all the CuI bands, with a few very weak and rather doubtful exceptions, can be arranged in five band-

<sup>16</sup> P. Kien, Diss. Bonn. 1908; Zeits. wiss. Phot. 6, 337 (1908).

systems, i.e., five complex groups of bands, each associated with a particular electronic transition in the CuI molecule, accompanied by a variety of vibrational transitions indicated by the values of the initial and final vibrational quantum numbers  $n'$  and  $n''$ . For simplicity, and in the absence of direct evidence from the present analysis, integral vibrational quantum numbers are here used in accordance with the usual practice, although the isotope effect in the BO spectrum<sup>17</sup> indicates that half-integral values may be needed. The assignment of vibrational quantum numbers is such as to satisfy the criteria used by Heurlinger and Kratzer, as well as the isotope effect criterion (I, p. 136).<sup>8</sup> The isotope effect, as previously emphasized,<sup>7,8</sup> was invaluable in locating the origins of the band-systems, giving, in fact, the first clue to the analysis of the very complex spectrum. In examining the arrangements of the bands in the tables, comparison with the reproduced spectrum (Plate I, and accompanying explanation) will be useful.

In Table VI are given, for each CuI system, equations in terms of the parameters  $n'$  and  $n''$  capable of representing within experimental error the positions of all the measured heads. The possibility that cubic

TABLE VI

*Equations representing CuI heads*

Note: the equations, except those for Cu<sup>63</sup>I, were obtained by plotting the appropriate first differences; the Cu<sup>63</sup>I coefficients were calculated according to theory from those of the corresponding Cu<sup>65</sup>I equations.

*A bands*

$$\begin{aligned}\text{Cu}^{63}\text{I}: \nu &= 19,707.65 + 211.91n' - 2.283n'^2 - 264.63n'' + 0.713n''^2 \\ [\text{Cu}^{65}\text{I}: \nu &= 19,707.7 + 209.72n' - 2.236n'^2 - 261.89n'' + 0.698n''^2]\end{aligned}$$

*B bands*

$$\text{Cu}^{63}\text{I}: \nu = 21,748.3 + 241.8n' - 1.88n'^2 - 265.4n'' + 1.0n''^2$$

*C bands*

$$\begin{aligned}\text{Cu}^{63}\text{I}: \nu &= 21,851.41 + 229.17n' - 0.447n'^2 - 263.86n'' + 0.653n''^2 \\ [\text{Cu}^{65}\text{I}: \nu &= 21,851.4 + 226.80n' - 0.438n'^2 - 261.14n'' + 0.640n''^2]\end{aligned}$$

*D bands*

$$\begin{aligned}\text{Cu}^{63}\text{I}: \nu &= 22,929.66 + F(n') - 264.2n'' + 0.64n''^2 \\ [\text{Cu}^{65}\text{I}: \nu &= 22,929.7 + 0.99F(n') - 261.5n'' + 0.63n''^2]\end{aligned}$$

Note:  $F(n') = 212.1$  for  $n' = 1$ .

*E bands*

$$\begin{aligned}\text{Cu}^{63}\text{I}: \nu &= 23,982.71 + 228.28n' - 0.954n'^2 - 263.81n'' + 0.671n''^2 \\ [\text{Cu}^{65}\text{I}: \nu &= 23,982.7 + 225.92n' - 0.934n'^2 - 261.09n'' + 0.657n''^2]\end{aligned}$$

terms in  $n'$  (and  $n''$ ) should be used has been disregarded, since the data are not precise enough to yield significant values of the coefficients of such terms. The coefficients, and especially the constants, of Table VI are, of course, somewhat influenced (cf I, pp. 131-2) by the fact that the

<sup>17</sup> R. S. Mulliken, Phys. Rev. 25,259 (March, 1925).



data refer to heads, instead of to origins (I, p. 123) or null-lines. This fact does not, however, obscure certain important major relations among the various bands. In fact, the present type of analysis, in which the arrangement of bands in systems is determined without regard to band-structure, seems to the writer a desirable preliminary, in complex cases like those of the copper halides, to a more detailed analysis of individual bands under higher dispersion.<sup>18</sup>

Considering for the present only the  $\text{Cu}^{63}\text{I}$  heads, one of the most striking facts revealed in Table VI is the near-identity of all coefficients of  $n''$  and  $n''^2$  for all five systems.<sup>19</sup> The agreement is so close as to make it extremely probable that the final electronic state (and associated vibrational states) are the same for all five systems. The differences in the coefficients and—what is more important—in the final state vibrational energy terms<sup>19</sup> for the different systems are small enough to be accounted for by the errors involved in their determination together with the fact that the coefficients and energy terms contain small contributions (I, p. 132) which differ from one system to another, due to the fact that the data refer to heads. The agreement is least good in the B system, where the reliable data are fewest. Granting that all five  $\text{CuI}$  band systems have the same final electronic state, it would seem that there is something peculiarly stable or normal about this state. There can, in fact, in view of the ready excitation of these bands and no others in the comparatively low temperature of the Bunsen flame,<sup>3</sup> taken together with the fact that they involve

<sup>18</sup> On p. 212 of Konen's book<sup>4</sup> the copper halide spectra are classed as "Pseudokanten-spektra" because the band heads become less and less conspicuous with increasing dispersion and in many cases finally disappear. On account of this behavior, Konen apparently considers it very doubtful whether the heads are genuine. The present analysis shows that the arrangement of the heads is completely in agreement with that found in other typical cases where no such question has been raised, and with that predicted by the quantum theory; also, the requirements of the isotope effect are completely satisfied. Hence the heads must be considered genuine. Their marked loss of conspicuousness under high dispersion is probably due to the close packing of the heads. This must result in the presence together at most points in the spectrum of series of structure lines from a number of different heads. When, under high dispersion, these are well resolved, the positions of individual heads, where new series begin, are naturally relatively inconspicuous. This is true especially of high-temperature spectra (flame or arc), where the series are prolonged. In active nitrogen the series are usually very short, corresponding to the low actual temperature. This tends to make the heads stand out much more sharply.

<sup>19</sup> The agreement is best brought out by comparing vibrational energy terms  $E''^m$ . These can be obtained from the original data or conveniently calculated from the equations of Table 6. Even for the larger values of  $n''$ , where  $E''^m = 2000$  to 4000 wave-number units, the maximum discrepancy between the energy terms for different systems is 4 units,—provided the comparison is restricted for each system to values of  $n''$  for which bands were actually measured.

initial state energies up to 3 volts in excess of the energy of the final state, be little doubt that this common final state is the normal state of the CuI molecule.

The near-equality of the  $n'$  coefficients for the A and D bands may be fortuitous or may indicate a relation between the two initial electronic states involved. The same is true in regard to the C and E bands. The agreement, it should be noted, does not extend to the coefficients of  $n'^2$ , at least in the latter case (in the former case the data are inadequate for decision).

The D bands are remarkable in that  $n'$  has only the values 0 and 1.<sup>20</sup> Presumably higher values of  $n'$  would involve instability of the molecule for the D electronic configuration.

In Fig. 2 the various electronic and vibrational levels revealed by the preceding analysis for Cu<sup>63</sup>I are arranged on a vertical wave-number scale; the arrangement is like that previously used in the case of BO.<sup>17</sup> At the right, the electron levels ( $N_0, A_0, \dots, E_0$ ) and their separations, are indicated. It should be recalled that the plotted values for the levels probably deviate slightly from the true values because the data used refer to heads. For Cu<sup>65</sup>I (not shown), the various electron levels coincide with those of Cu<sup>63</sup>I, but each set of vibrational levels has a somewhat smaller spacing, in accordance with the equations of Table VI.

It will be noted that in all five CuI systems the vibration frequency is less for the excited than for the normal electronic state. Although the individual bands are not resolved, the fact that they are all shaded toward the red is enough to show (cf Sommerfeld, *Atombau und Spektrallinien*, 4th ed., chap. IX, §3) that the interatomic distance and moment of inertia are greater, in all five systems, for the excited state than for the normal state of the molecule. The above facts both indicate weaker binding forces for the excited electronic states than for the normal state of CuI. The CuBr and CuCl bands disclose analogous relations for these molecules. The correlation of increased moment of inertia with decreased vibration frequency (or vice versa) when a molecular electron is excited is, as Birge has pointed out, a rule without known exception.<sup>21</sup>

*Analysis of CuBr and CuCl Spectra.* Most of the strongest CuCl heads (mostly the first head of each group) were arranged by Derichsweiler<sup>5</sup> in two long series (I and II) of approximately equally spaced heads. The same is true of CuBr. In each series the intensity is somewhat

<sup>20</sup> There are one or two doubtful and very weak bands for which, possibly,  $n' = 2$ .

<sup>21</sup> R. T. Birge, paper before American Physical Society (abstract No. 23, *Phys. Rev.* **25**, 240, 1925). The question of intensity distribution with respect to  $\Delta n$  and to  $n'$  was also discussed in this paper.

undulating, with two principal maxima. Corresponding members of series I and II form characteristic pairs of heads. In the case of CuI (cf. Table VII below), according to Derichsweiler, series II is nearly absent. The present analysis shows that Derichsweiler's arrangement into series has very little significance. In reality the spectrum of CuBr consists probably of four, that of CuCl of six (one closely double) different systems of bands, in part closely intermingled, giving rise to the appearance of pairs of heads.<sup>18</sup> Preliminary study indicates that, as with CuI, the several systems of each compound have a common final state.

#### CONFIRMATION OF VIBRATIONAL ISOTOPE EFFECT

In the reproductions of Plate I, practically all the Cu<sup>63</sup>I heads recorded in Tables I-V are marked. The corresponding weaker Cu<sup>65</sup>I heads are not marked, but many of them can be located by comparison with the tables. It will be seen that they are arranged entirely as would be expected (cf. theoretical diagram, I, p. 129). The Cu<sup>65</sup>I bands are especially well shown at the low-frequency end of the A system. In the region near the origin of each system, the heads of the two isotopes are of course not resolved. On the high-frequency side of the origin, the Cu<sup>65</sup>I heads are partially or wholly obscured, each by the shading from the adjacent Cu<sup>63</sup>I head.

In order to consider the question quantitatively, let us suppose that one of two isotopic molecules emits a system of bands, the wave-numbers of whose origins can be expressed by an equation of the form

$$\nu_1 = \nu^0 + a'n' - b'n'^2 - a''n'' + b''n''^2 \quad (1)$$

Then for the other isotope, according to theory (I, p. 127),

$$\nu_2 = \nu^0 + \rho a'n' - \rho^2 b'n'^2 - \rho a''n'' + \rho^2 b''n''^2 \quad (2)$$

Here  $\rho = \sqrt{\mu_1/\mu_2}$ ,  $\mu_1$  and  $\mu_2$  being the respective reduced masses. In case one has data on band-heads, instead of on origins, small contributions are added to all the terms of Eq. (1); and since these are subject to the *rotational* isotope effect, which differs from the vibrational effect, the relation of  $\nu_2$  to  $\nu_1$  is slightly altered. In respect to the terms depending on  $n'$  and  $n''$ , the effect should be negligible (I, p. 132) as compared with experimental error. In respect to the constant term, a small but perhaps appreciable effect is to be expected.<sup>22</sup>

<sup>22</sup> The fact that the data of Tables I-V are on heads, instead of on origins, involves the possibility of a slight shift of all the Cu<sup>65</sup>I heads with respect to the Cu<sup>63</sup>I heads. For the constant term of Eq. 1 now represents not  $\nu^0$  alone (for which no appreciable isotope effect is to be expected: (I, p. 124-5)), but  $\nu^0 + \nu_{head}$ , where  $\nu_{head}$  is the distance from the origin to the head of the band for which  $n'$  and  $n''$  are both zero. Corresponding to  $\nu_{head}$  there must be a rotational isotopic displacement of approximately  $(\rho^2 - 1)\nu_{head}$ .

If  $\nu_1$  refers of  $\text{Cu}^{63}\text{I}$ , then for  $\text{Cu}^{65}\text{I}$  as compared with  $\text{Cu}^{63}\text{I}$ ,  $\rho = 0.98966$ , and  $\rho^2 = 0.97943$ . From the  $\text{Cu}^{63}\text{I}$  coefficients in the equations of Table VI, the corresponding theoretical values of the  $\text{Cu}^{65}\text{I}$  coefficients can be calculated. The equations so obtained have been given in Table VI. From these the theoretical positions of all the  $\text{Cu}^{65}\text{I}$  heads can be calculated. These predicted values can then be compared with the experimental data. It is most convenient to do this by comparing calculated with observed values of the *isotopic displacement*,  $(\nu_2 - \nu_1)$ , as is done in Tables I-V. The result is complete agreement, within experimental error, for the entire range of  $n'$  and  $n''$  values in all the systems, so far as data could be obtained.<sup>22,23</sup> The slight average deficiency in the observed as compared with the calculated isotopic displacements for the E bands is probably within experimental error, but is in the direction to be expected<sup>22</sup> from the fact that the measurements were on heads. The data are not accurate enough to furnish evidence on the question of half-integral vibrational quantum numbers.<sup>22</sup>

#### INTENSITY DISTRIBUTION IN THE $\text{CuI}$ BANDS

In a system of bands, the distribution of intensity with respect to  $n'$  and  $n''$  is of interest chiefly from two points of view, distribution with

(I, p. 131). In the  $\text{CuI}$  bands,  $\nu_{\text{head}}$  is always positive, since the heads are shaded toward the red. Hence, since  $(\rho^2 - 1)$  is negative here, this rotational contribution to  $(\nu_2 - \nu_1)$  must be negative; its magnitude, of course, cannot be determined without analysis of the band structure. In the equations of Table VI and the calculated isotopic displacements of Tables I-V, no allowance was made for this contribution. If it is appreciable, it should therefore be evident by an appreciable negative value for the average observed minus the average calculated isotopic displacement.

If, as is apparently true in  $\text{BO}$ ,<sup>17</sup> the true minimum values of  $n'$  and  $n''$  are  $1/2$  instead of 0 as assumed throughout the preceding discussion, the bands here assumed to have  $n' = n'' = 0$ , and so the constants of the equations of Table VI, should be subject to a vibrational isotopic displacement  $(\nu_2 - \nu_1)$  of  $+0.28$  units for the A bands, and  $+0.18$  units for the E bands. These effects are accordingly of opposite sign to the rotational head effect discussed in the preceding paragraph. The calculated net effects should be: A bands,  $+0.28 - x$ ; E bands,  $+0.18 - y$ . The observed effects are: A bands,  $+0.05$ ; E bands,  $-0.4$ . It will be seen that the observed effects do not contradict the existence of half quantum numbers. The relatively large experimental error, the possibility of relative error, due to differences in intensity, etc., in setting on the heads of the two isotopes, and the fact that  $x$  and  $y$  are unknown, make it impossible, however, to draw any positive conclusions.

<sup>23</sup> The confirmation of the theory is of course not nearly as exact as in the case of  $\text{BO}$ ,<sup>17</sup> on account of the much smaller values of the isotopic displacements.

In the case of  $\text{BO}$ , equations for  $\nu_1$  and  $\nu_2$  were obtained independently from the experimental data, and their coefficients compared. This is a rather more rigorous test than that here applied; but unless the data used are equally complete and accurate for both isotopes, it is one which is likely to disguise somewhat the real agreement with theory.

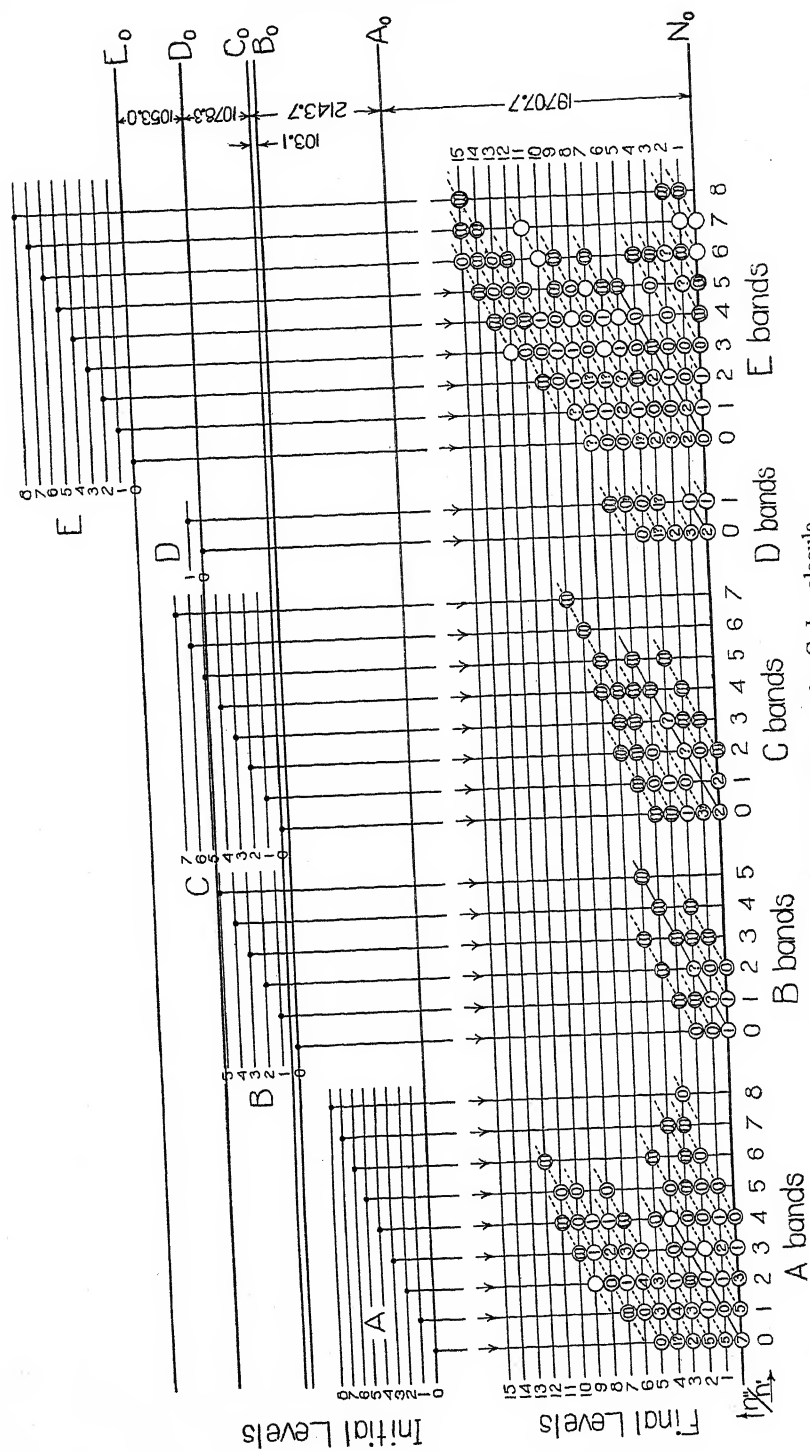


Fig. 2. Energy level diagram for  $\text{CuI}$  molecule.

Fig. 2. Energy level diagram for CuI molecule.—The electronic and vibrational energy levels found by analysis of the CuI band spectrum are shown on a vertical wave-number scale. Each electronic level ( $N_0$ , the normal level,  $A_0, B_0, \dots$ , excited levels) is shown by a heavy horizontal line; above it the correlated vibrational levels are shown. In the case of the excited electronic states, the lines for the vibrational levels are drawn only part way across the diagram, in order to avoid confusion. Rotational levels are not shown. The A bands correspond to transitions from A levels to N levels, the B bands to transitions from B to N levels, and so on. Each observed band is indicated by a circle near the lower end of a vertical line, the figure in the circle denoting intensity; where the figure is omitted, the intensity is very low (000). Diagonal lines are used to indicate band-sequences, the full-line diagonal representing the (0) sequence. The spacing of the electron levels is indicated at the right.

respect to  $\Delta n$  ( $\Delta n = n'' - n'$ ), and with respect to  $n'$ . The former is a matter of transition probability, depending on several factors recently discussed by Lenz in relation to the correspondence principle.<sup>24</sup> The latter probably depends chiefly on the initial distribution of excited molecules among various  $n'$  values, and so gives a means of studying the  $n'$  distribution. In the case of CuI, Fig. 2 gives a good idea of these distributions for each of the five systems of bands. Each diagonal line serves to mark out a "band-sequence," i.e., a set of bands of given  $\Delta n$ ; each vertical line marks a set of given  $n'$ . By comparison of adjacent diagonal or vertical sets, respectively, the  $\Delta n$  or  $n'$  distribution can be studied.

For thermal equilibrium, the number  $N_n$  of molecules having a given value  $n$  of the vibrational quantum number  $n'$ , and a corresponding energy  $E_n$ , should be proportional to  $e^{-E_n/kT}$ . Assuming, as an approximate average value for the five systems,  $E_n = 225n$  (wave-number units), taking  $k$  in the same units ( $k = 0.698$ ), and assuming  $T = 373^\circ\text{K}$ ,  $N_n$  is proportional to  $e^{-0.865n}$ . For  $n = 0, 1, 2, 3, 4, 5, \dots$  this gives values of  $N_n$  proportional to 1, 0.42, 0.177, 0.075, 0.032, 0.013,  $\dots$ . No more than a rough qualitative comparison is possible with the recorded intensities of Tables I-V and Fig. 2. However, it will be seen that in all five systems there is a steady falling off of intensity from  $n' = 0$ —except, as previously noted, that the  $D$  bands are completely cut off above  $n' = 1$ —at a rate which seems to be in accord with the preceding calculations, corresponding to a low temperature.

The above result is in contrast to that previously observed<sup>17</sup> in the case of the  $\alpha$  and  $\beta$  systems of BO. For BO,  $E_n$  is approximately  $1260n$ , so that the  $N_n$  values should fall off very rapidly, in proportion to  $e^{-4.85n}$  for equilibrium at  $100^\circ\text{C}$ . For  $n' = 0, 1, 2, \dots$  they should then be proportional to 1, 0.0079, 0.00006,  $\dots$ . Actually, the  $n' = 0$

<sup>24</sup> W. Lenz, *Zeits. f. Phys.* **25**, 299 (1924). Cf also T. Heurlinger, *Zeits. f. Phys.* **1**, 82 (1920).

series are less intense than some of the others, the intensity maximum being near  $n'=2$ ; in addition, bands with  $n'$  values as high as 8 were observed, which would obviously be impossible for thermal equilibrium. Non-thermal and high-temperature vibrational energy distributions occur in other cases of band spectra excited by active nitrogen, e.g., in the CN and SiN bands. In the case of the NO  $\beta$  bands ( $\beta$  bands of active nitrogen), as Birge has recently pointed out,<sup>21</sup> the distribution corresponds more nearly to equilibrium at the (low) temperature of active nitrogen. Further discussion of these points will be found in the paper<sup>17</sup> on BO.

The distribution with respect to  $\Delta n$  in the CuI bands considerably resembles that in the  $\beta$  bands of BO.  $\Delta n$  ranges from perhaps  $-6$  to  $+9$ , and, although there is some approach to the symmetry about  $\Delta n=0$  which is predicted by Lenz's theory,<sup>24</sup> there is an obvious preference for positive  $\Delta n$  values.<sup>25</sup> Another characteristic feature, noted here and in both  $\alpha$  and  $\beta$  systems of BO, and perhaps typical of band spectra in general,<sup>21</sup> is the tendency for numerically large  $\Delta n$  values to be associated with large  $n'$  values. Although Lenz does not refer to it, this effect, as also the preference for positive  $\Delta n$  values, appears to be predictable from his theoretical treatment; for the occurrence of large values of  $\Delta n$  is there connected with the existence of considerable perturbations of the electronic motion by the vibrational motion of the nuclei; and the magnitude of such perturbations must increase with the value of  $n$ , which determines the amplitude of vibration. Hence large values of  $n'$  should favor large values of  $\Delta n$ , and also, since the motion of the emitting electron in both initial and final states of the molecule must be considered in Lenz's application of the correspondence principle, should favor positive values of  $\Delta n$ , since for these  $n''$  is also large.

The association of large  $n'$  with large  $\Delta n$  values has a striking effect on the appearance of band sequences in cases, like those of the copper halides, where the members of a sequence follow one another in close succession (cf. Plate I). In the sequences near the origin, i.e., those for which  $|\Delta n|$  is small, each sequence begins with an intense head—for which either  $n'$  or  $n''$  is zero—the succeeding heads being progressively less intense.<sup>26</sup> Farther from the origin, the intensity maxi-

<sup>25</sup> This is probably *not* due primarily to variations in plate sensitivity and prism transmission, although of course these must have a marked distorting influence.

<sup>26</sup> Exceptions to this rule of progressive decrease sometimes occur due to abnormally low intensity of particular bands. Thus (cf. Plate I) the  $\Delta n=0$  sequence of the E bands starts out with a weak (0,0) head, while the  $\Delta n=+1$  sequence has a weak spot at the (1,2) band; again, the A sequence for which  $\Delta n=0$  has a weak spot at (1,1), followed by a revival with (2,2).



mum shifts away from the first head, and in the highest-numbered sequences the first few heads may become too weak to be detected (cf. Plate I and Fig. 2, A and E bands). Konen noted this effect in the copper halide bands, and gives a good diagram<sup>4</sup> illustrating it in the case of some of the CuCl bands; certain fluoride bands also show it well. This phenomenon is particularly well marked in the positive sequences ( $\Delta n$  positive). Here the first head of each sequence corresponds necessarily to  $n' = 0$ , whereas in the negative sequences, the value of  $n'$  for the first head is necessarily the same as  $|\Delta n|$ .

Attention may be called to the A bands of CuI as a typical example, with respect to arrangement and intensity distribution, of a well-developed band system. The A bands also illustrate well the abrupt change of spacing for the strong first heads of successive sequences, at the origin of the system. These points appear to good advantage in Plate I on account of the freedom from marked variation of photographic sensitivity and from overlapping by other band-systems, in the region occupied by the A bands. The absence of resolution of the bands into structure lines also helps to make clear the arrangement of the bands.

#### COMPARISON WITH DATA OF PREVIOUS INVESTIGATORS

Data in the literature on complex band spectra often refer to the first head only of each of the more obvious sequences. This is illustrated in Table VII, where the data of previous observers on the CuI bands are

TABLE VII

*Comparison with previous data*

Previous data (wave-lengths)*			Present identification
M.	D.	E.&V.	
5393	—	—	A sequence 5354-5419
5314	—	5330	" " 5282-5364
—	—	5250	?
5232	—	—	A sequence 5211-5241
—	5210(I)	5210	Head 0,2 A, 5210.7
5144	5141(I)	5142	" 0,1 A, 5141.1
—	—	5106	" 2,2 A, 5101.9
5073	5072(I)	5075	" 0,0 A, 5072.8
5018	5019(II)	—	" 1,0 A, 5019.7
4959	—	—	" 2,0 A, 4968.3(?)
—	4883(II)	—	A sequence 4873-4930
—	4826?(II)	—	?
—	4769(II)	4760	C sequence 4744(?)
—	4710(II)	—	Head 0,2 B, 4711.3
—	4686(I)	4685	" 0,2 C, 4686.8 and 4687.8
—	4631(I)	4630	" 0,1 C, 4630.6
—	4575(I)	4575	" 0,0 C, 4575.2

\* M. = Mitscherlich (wave-lengths calculated by Watts in his "Index of Spectra" from photograph by Mitscherlich); D. = Derichsweiler (Roman numerals in parentheses after wave-lengths denote series of Derichsweiler<sup>5</sup>); E. & V. = Eder and Valenta.<sup>6</sup>



TABLE VII—continued

4523(I)	4523	Head 1,0 C, 4527.9
4462(?) (I)	4464	" 0,2 D, 4462.2, and 1,7 E, 4463.6
4409(I)	4408	" 0,5 E, 4408.1
4358(I)	4358	" 0,4 E, 4358.3; 0,0 D, 4360.0; 1,5 E, 4364.0
—	4323	?
—	4320	" 1,0 D, 4320.0
4309(I)	—	" 0,3 E, 4308.2 and 4309.6
—	4280	" 3,5 E, 4280.1
4261(I)	4261	" 0,2 E, 4261.7
4214(I)	4213	" 0,1 E, 4214.6
4169(I)	4172	" 0,0 E, 4168.5 or 1,1 E, 4174.6
4126(I)	4130	" 1,0 E, 4129.4
—	4098	" 2,0 E, 4091.3

compared with the present data. In the higher-numbered sequences, the first head becomes too faint to be noticed, and a rough measurement of the beginning or middle of the region of maximum intensity is likely to be given; obviously such data are of almost no value from a theoretical standpoint.

For the first head of a sequence, either  $n'$  or  $n''=0$ . On the low-frequency side of the origin ( $n', n''=0$ ), in each CuI system, these form a series ( $n', n''$ ) = (0, 0), (0, 1), (0, 2), . . . with a nearly constant first difference of somewhat over 260 wave-number units, common to all five systems on account of their common final electronic state. Derichsweiler's series I for CuI is made up chiefly of the E bands (0, 0), (0, 1), . . . (0, 5) and the C bands (0, 0), (0, 1), (0, 2), pieced together by (0, 2) D and (1, 0) C, which, however, of course do not fit in very well (this was explained by Derichsweiler as perhaps due to inaccuracies of measurement). After a gap containing miscellaneous bands grouped as series II, series I reappears with (0, 0), (0, 1), and (0, 2) of the A system.

#### THE EXCITATION OF SPECTRA BY ACTIVE NITROGEN

The suggestion has been made by several writers<sup>27,28,29</sup> that the excitation of spectra by active nitrogen is the result of "collisions of the

<sup>27</sup> R. T. Birge: cf. abstract, Phys. Rev. 23, 295 (1924); Nature, Nov. 1, 1924.

<sup>28</sup> R. S. Mulliken, loc. cit.;<sup>7</sup> Nature, Sept. 6, 1924; Phys. Rev. 25, 278 (1925).

<sup>29</sup> M. N. Saha and N. K. Sur, Phil. Mag. 48, 421 (1924). It should be pointed out that this paper contains certain errors in the interpretation of the band spectra appearing in active nitrogen, and in the estimated energy of the latter. These have been corrected in Birge's letter <sup>27</sup> to Nature. See also Foote and Ruark, Nature, Nov. 22, 1924, and Foote, Ruark, and Chenault, (abstract, Phys. Rev. 25, 241, 1925) who discuss the excitation of the spectrum of mercury by active nitrogen. The present writer believes that Birge's estimate of about 11.5 volts, for the energy of active nitrogen in the state which immediately precedes the emission of the characteristic visible afterglow bands, should be reduced to 10.4 volts (this point will be discussed elsewhere). The true energy may be somewhat different, however, probably higher, since the active nitrogen must be in a metastable state<sup>27</sup> which presumably differs from the emitting state, although Birge assumes the two to be identical.

second kind," analogous to the action of excited mercury atoms in the work of Franck and Cario.<sup>30</sup> The effects are, however, much more varied in active nitrogen than with excited mercury atoms. The excitation of atomic spectra by active nitrogen, as studied experimentally by E. P. Lewis<sup>31</sup> and by Rayleigh and Fowler,<sup>32</sup> has been discussed in some detail by Saha and Sur.<sup>29</sup>

The behavior of the copper halides in active nitrogen illustrates particularly two characteristic modes of action of the latter. As indicated in the preliminary abstract,<sup>7</sup> it appears that excited  $N_2$  molecules may either (a) excite molecular electrons so as to give rise to the emission of the halide band spectra, or (b) dissociate the halide molecules. The excitation of atomic spectra is also illustrated, excitation of the copper and halogen atoms possibly accompanying but probably following the dissociation. Another possibility referred to in the abstract, namely reaction with the halide molecule to form copper nitride, must now be regarded as very doubtful (see under "oxide bands" in introduction), although the analogous process occurs in many other cases, e.g.,<sup>33</sup> formation of CN and SiN, respectively, by reaction of  $N_2'$  molecules (the prime will be used to denote an excited atom or molecule) with carbon and silicon compounds. Other interesting reactions are the appearance of the NO bands<sup>33</sup> on admission of  $O_2$  or other oxygen compounds into active nitrogen, and of the CN and NO bands (also probable CO bands) on admission of CO. Possible formulations of these reactions are  $O_2 + N_2' \rightarrow NO' + NO$ , and  $CO + N_2' \rightarrow CN' + NO$ , or  $CN + NO'$ .

In the case of the copper halides, the occurrence in high intensity of the copper arc spectrum (over 80 lines were identified) and of the intense iodine arc line<sup>34</sup> at  $\lambda 2062$  when CuI was used, indicate that excited Cu

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The subject of active nitrogen has also been discussed by N. R. Dhar (J. Phys. Chem. **28**, 948, 1924).

<sup>30</sup> Franck and Cario, Zeits. f. Physik **9**, 259; **10**, 185; **11**, 161 (1922); **17**, 202 (1923).

<sup>31</sup> E. P. Lewis, Astrophys. J. **20**, 49 and 58 (1904); Phil. Mag. **25**, 826 (1913); and other papers.

<sup>32</sup> Ref. 10 and later papers in Proc. Roy. Soc.

<sup>33</sup> See R. S. Mulliken, Phys. Rev. **25**, 277-8, 290, and references there cited.

<sup>34</sup> C. Füchtbauer, F. Waibel, and E. Holm found this line strongly absorbed in atomic iodine at 1000°C (Zeits. f. Phys. **29**, 367, 1924). Their measured wave-length was  $\lambda_{vac.} = 2062.1 \pm 0.1$ . An approximate measurement by the writer on the emission line obtained from CuI gave  $\lambda_{vac.} = 2062.3$ . W. Gerlach and F. Gromann (Naturw. **12**, 578, 1924) had previously reported a line at  $\lambda 2063$  absorbed by partly dissociated iodine at 150°C, but their result is less conclusive than Füchtbauer's on account of the probable molecular absorption. A strong emission line at  $\lambda 2064$  reported by O. Oldenberg (Zeits. f. Phys. **18**, 7, 1923), and at  $206m\mu$  by Ludlam and West (Nature **113**, 389, 1924), is without doubt identical with that here under discussion. The nature of  $\lambda 2062$  has also been discussed recently by L. A. Turner and K. T. Compton (Phys. Rev. **25**, 791, 1925).

and I atoms are formed in large numbers as a direct or indirect result of process (b) above. Exactly the same set of Cu lines is obtained, with the same relative intensities, so far as could be judged from inspection of the photographs, whether CuCl or CuI is used (and so far as could be seen in a short exposure, the same as with CuBr). According to Dr. A. G. Shenstone, who was so kind as to examine the data, the entire arc spectrum appears to be present, and in addition a group of lines whose initial state corresponds to a slightly negative term, hence presumably to simultaneous excitation of two electrons. The spectrum differs markedly in intensity distribution from that of the ordinary copper arc.

It may be noted that there was no trace, when CuI was used, of the intense band spectrum which is excited when iodine ( $I_2$ ) is admitted to active nitrogen.

Since CuCl is known to be largely or completely associated to  $Cu_2Cl_2$  in the vapor state<sup>35</sup> (presumably CuBr and CuI also are associated), it is not possible at present to specify definitely the details of processes (a) and (b) above. It is likely that the formation of  $CuX'$  molecules and  $Cu'$  and  $X'$  atoms by the interaction of  $N_2'$  molecules and  $CuX$  or  $Cu_2X_2$  molecules occurs in a number of different ways. The category of possible modes of dissociation and excitation is of course limited to processes in which the expenditure of energy does not exceed the initial energy of the  $N_2'$  molecule (plus a small contribution due to energy of relative translation of the impinging molecules); this initial energy corresponds probably to 10.4 volts or a little more.<sup>29</sup>

The formation of  $CuX'$  molecules might occur directly from  $Cu_2X_2$  and  $N_2'$ , or might require the intermediate formation of unexcited  $CuX$  molecules. Similarly the formation of Cu and X atoms from  $Cu_2X_2$  might occur in one or in two steps, and the formation of  $Cu'$  and  $X'$  atoms in from one to three steps. In any case there are three distinct possibilities as to the mode of excitation of the Cu and X atoms: (1), the dissociation of  $Cu_2X_2$  or  $CuX$  molecules may yield neutral unexcited atoms, excitation of these occurring in subsequent impacts with  $N_2'$  molecules; (2), excitation may occur simultaneously with dissociation; (3), the dissociation may yield the ions  $Cu^+$  and  $X^-$ . Since the ionization potential of Cu is about 7.7 volts, the energy of  $N_2'$  is considerably more than enough for the excitation of the entire arc spectrum of Cu in secondary impacts of Cu with  $N_2'$  in connection with (1); further, the excited spectrum should be the same for all three halides, as is the case for the observa-

<sup>35</sup> See von Wartenberg and Bosse, *Zeits. f. Elektrochem.* **28**, 384 (1922).

tions reported above. In process (2) the energy required includes a heat of dissociation in addition to the energy of excitation. The heat of dissociation may be estimated<sup>36</sup> at 2 or 3 volts for CuX, so that excitation of the entire arc spectrum might still be possible. It would, however, be strange if there were not then differences in intensity distribution, contrary to the observed facts, for the different halides. Dissociation of Cu<sub>2</sub>X<sub>2</sub> in any manner, with simultaneous excitation of Cu atoms to give the entire arc spectrum, must probably be ruled out on account of the large energy required for dissociation.<sup>36</sup> Process (3), followed by reunion of an electron with a Cu<sup>+</sup> ion, should like process (1) give the same Cu spectrum for all the halides, in accord with observation. The energy required for (3) would not be excessive<sup>37</sup> for dissociation of CuX, but might be too great for the reaction Cu<sub>2</sub>X<sub>2</sub> → CuX + Cu<sup>+</sup> + X<sup>-</sup>. On the whole, the evidence is decidedly against (2), and in favor of (1) or (3), as the main factor in the formation of excited Cu atoms. Energy considerations favor (1) as against (3) if the dissociation of Cu<sub>2</sub>X<sub>2</sub> occurs in one step; the fact that the system Cu + X has less energy than Cu<sup>+</sup> + X<sup>-</sup> also indicates it to be a more likely result of dissociation. For the formation of X' atoms only (1) is possible.

The increasing relative intensity of the Cu line spectrum, as compared with the CuX band spectrum, in going from CuCl to CuI, may be ascribed to an increasing probability of dissociating rather than exciting the CuX molecule, correlated with the decreasing chemical stability of the molecules in this order.

There is a possibility that CuX<sub>2</sub> molecules may be important in the excitation of the spectra of the Cu halides by active nitrogen, although

<sup>36</sup> Assuming that all three cuprous halides are present in the vapor state chiefly as double molecules, the following approximate values for the heat of dissociation into unexcited neutral atoms can be calculated from thermochemical<sup>35</sup> and electron affinity data: Cu<sub>2</sub>Cl<sub>2</sub>, 10.2 volts, Cu<sub>2</sub>Br<sub>2</sub>, 9.1 v, Cu<sub>2</sub>I<sub>2</sub>, 8.3 v, using the value 68 kg.-cal. per mol for the heat of vaporization of Cu (cf R. W. Millar, *Ind. Eng. Chem.* **17**, 34, 1925). The heat of dissociation of CuX into atoms and of Cu<sub>2</sub>X<sub>2</sub> into 2 CuX are unknown, but may be estimated by assuming that the former is the same as for AgX (which does not form double molecules in the vapor state). The writer is indebted to Dr. R. H. Gerke for this suggestion. For AgCl vapor, the heat of dissociation into atoms is equivalent to about 3.3 volts, for AgI to about 2.2v (cf. R. H. Gerke, *J. Am. Chem. Soc.* **46**, 953, 1924; also von Wartenberg and associates, *Zeits. f. Elektrochem.* **27**, 162, 568, 1921, and **28**, 284, 1922). Assuming the same values for CuCl and CuI, the heat required for Cu<sub>2</sub>X<sub>2</sub> → 2CuX is then equivalent to 3.6v for CuCl and 3.9v for CuI.

<sup>37</sup> Gerke (l.c.<sup>36</sup>) points out that for halogen salts the heat of dissociation is approximately equal to the electron affinity of the halogen. A corollary of this is that the heat of dissociation of such salts into ions must be about equal to the ionizing potential of the metal.

the weight of chemical evidence indicates that  $\text{CuX}_2$  is decomposed to  $\text{Cu}_2\text{X}_2$  and  $\text{X}_2$  in the process of vaporization. In the present work, both  $\text{CuCl}_2$  and  $\text{Cu}_2\text{Cl}_2$  were used, but no obvious differences in relative intensities of different bands, or of the bands as compared with the Cu lines, were observed.

*Mercury halides.* Some experiments of the writer on the excitation of spectra of certain volatile salts by active nitrogen are of interest here.  $\text{PbI}_2$ ,  $\text{HgI}_2$ , and  $\text{HgBr}_2$  have been tried.<sup>38</sup> Each gives the arc spectrum of the metal, well developed, also  $\lambda 2062$  and other I arc lines<sup>38</sup> in the case of the iodides, and characteristic halide bands in each case (very weak in the case of  $\text{PbI}_2$ , strong in the other two cases). The band spectra appear to be rather complex, suggesting triatomic emitters  $\text{MX}_2$ , but it seems more likely that they are due to diatomic emitters  $\text{MX}$ , in which case the complexity may be due to the presence of several superposed systems of bands as in the  $\text{CuX}$  spectra. In the case of the two Hg salts, the complete arc spectrum of Hg appears to be developed; thus diffuse series lines are present at least up to  $2p_1-6d$ ; the  $6d$  terms correspond to an energy of 10.0 volts, only 0.4 v short of ionization. In both cases the intensity distribution appeared to be closely similar to that in other experiments where Hg alone was used (except that  $\lambda 2537$  was relatively much weaker in the latter case, presumably because of greater absorption).<sup>38</sup> These results parallel those with  $\text{CuCl}$  and  $\text{CuI}$ , and lead to similar conclusions, except that process (1), dissociation into unexcited atoms, is even more definitely indicated here, on account of the high ionizing potential of Hg, as the chief factor. The formation of  $\text{Hg}^+$  ions, probably by the reaction  $\text{Hg} + \text{N}_2' \rightarrow \text{Hg}^+ + \text{N}_2 + e$ , is indicated by the (rather weak) presence of the Hg spark line  $\lambda 1942$  (the emission of this line would follow the secondary process  $\text{Hg}^+ + \text{N}_2' \rightarrow \text{Hg}^{+*} + \text{N}_2$ ).

The study of the excitation of spectra by active nitrogen is being continued, and a further discussion will be given later.

<sup>38</sup> In some of the experiments with the iodides, the characteristic banded structure beginning near  $\lambda 3450$ , which results<sup>10</sup> from the action of  $\text{N}_2$  (or a suitable electrical discharge) on  $\text{I}_2$ , was present. This was probably due to partial decomposition of the iodide before its entrance into the active nitrogen, or in part to secondary formation of  $\text{I}_2$  from I atoms, rather than to direct formation of  $\text{I}_2$  or  $\text{I}_2'$  molecules by dissociation. The spectrum of  $\text{HgI}_2$  in active nitrogen was earlier examined by Rayleigh and Fowler<sup>10</sup>, who found this iodine band fairly prominent. Of the Hg line spectrum, they noted only  $\lambda 2537$ ; this result was probably due to an exposure insufficient to bring out the other lines, since in the present work  $\lambda 2537$  was found to be much more prominent than the latter.—In the present work with the iodides (and iodine) several additional lines, evidently iodine arc lines, were noted (cf. abstract of paper by R. S. Mulliken and L. A. Turner, *Phys. Rev.* 25, 886, 1925).

NATURE OF EXCITED ELECTRONIC STATES IN COPPER HALIDE  
MOLECULES, AND THE BAND SPECTRA OF  
POLAR COMPOUNDS

The nature of the electronic changes involved in the excitation of the  $\text{CuX}$  molecule ( $\text{X}$  = any halogen) will now be considered briefly. Since  $\text{CuX}$  is of a polar or ionic type—although less definitely so than compounds like  $\text{NaCl}$ —the excited electron must probably belong either to the  $\text{Cu}^+$  ion or to the  $\text{X}^-$  ion. Excitation of an  $\text{X}^-$  electron in  $\text{Cu}^+\text{X}^-$  by impact with a free electron or excited atom or molecule would presumably mean complete loss of this electron to the  $\text{Cu}^+$  ion, since outer quantized orbits are hardly to be expected for this electron in the  $\text{X}^-$  ion. The  $\text{Cu}$  atom would thus be left in its normal state, or, if enough energy were supplied, in one of several excited states; and the  $\text{Cu}$  and  $\text{X}$  atoms would be left clinging together by virtue of secondary forces as a non-ionic molecule  $\text{CuX}$ . From this condition they might undergo, as the result of the impact of a third molecule, either the change  $\text{CuX} \rightarrow \text{Cu} + \text{X}$ , or (cf. Born and Franck, ref.<sup>39</sup>)  $\text{CuX} \rightarrow \text{Cu}^+\text{X}^-$ . The spontaneous occurrence, with the emission of a band spectrum, of the reaction  $\text{CuX}$  or  $\text{Cu}'\text{X} \rightarrow \text{Cu}^+\text{X}^-$  is conceivable, but must probably be ruled out.<sup>39</sup> Another possibility is that, in the presence of a  $\text{Cu}^+$  ion, the  $\text{I}^-$  ion would be so greatly deformed that a series of quantized states for an  $\text{I}^-$  electron could occur, resembling those in an  $\text{I}$  atom. It is more probable, however, that the observed group of five electron levels in the  $\text{CuI}$  molecule corresponds to excitation of the  $\text{Cu}^+$  ion. The five  $\text{CuI}$  band-systems should then be analogous to the most easily excited lines of the  $\text{Cu}^+$  spectrum. This spectrum should contain odd-numbered multiplets. The group of  $\text{CuI}$  levels  $\text{A}_0$  to  $\text{E}_0$  might then correspond to a multiple term of  $\text{Cu}^+$ , considerably modified, of course, and perhaps increased in complexity, by the presence of the  $\text{I}^-$  ion.

That the  $\text{Cu}^+$  ion contains an easily excited electron or electrons is indicated by the existence of salts in which the  $\text{Cu}$  atom has a valence of two, showing that the  $\text{Cu}^+$  ion in  $\text{Cu}^+\text{X}^-$  has an electron which is easily transferred to a halogen atom to form  $\text{Cu}^{++}\text{X}_2$ . The process of complete transfer of a  $\text{Cu}^+$  electron to an  $\text{X}$  atom is of course markedly different from the mere excitation of a  $\text{Cu}^+$  electron in  $\text{Cu}^+\text{X}^-$ ; it may be described as an induced ionization, being assisted by the electron affinity of the  $\text{X}$

<sup>39</sup> M. Born and J. Franck (Ann. der Physik, 76, 229, 1925) have concluded that the emission of radiation in such a process is, on correspondence principle grounds, not to be expected. The same would apply to the converse process of excitation of the molecule by absorption of radiation. See also their important article in Zeits. f. Phys. 31, 411 (1925).



atom. Excitation of a  $\text{Cu}^+$  electron in  $\text{Cu}^+\text{X}^-$ , and complete transfer as in  $\text{Cu}^+\text{X}^- + \text{X} \rightarrow \text{Cu}^{++}\text{X}^{-2}$ , stand, however, in much the same relation as excitation and ionization of an electron in a single atom. Since in general low ionization potentials involve low resonance potentials, the above correlation of  $\text{CuX}_2$  formation with  $\text{CuX}$  excitation seems justified.

In the same connection it is noteworthy that the halides of those metals which show a valence only of one give no electronic band spectra. In this class are the halides of the alkali metals (and hydrogen).<sup>40</sup> The absence of a valence of two in these cases must depend mainly on the absence of a low enough ionization potential for the positively charged ion ( $\text{M}^+$ ) of the metal. It is especially notable that silver, which belongs in the same group of the periodic system as copper but fails to show a valence of more than one, also fails<sup>40</sup> to give halide band spectra. Gold, also in the same group, shows valences of one and three, and gives halide spectra. It may be that in polar compounds the molecule is incapable of carrying electronic energy much in excess of the heat of dissociation into atoms, any attempt to impart larger amounts of energy resulting, either spontaneously, or as an indirect result of the formation of an excited molecule of a type highly sensitive to encounters with other molecules, in prompt dissociation.<sup>41</sup> The heat of dissociation into atoms corresponds to between 3 and 6 volts for the various alkali and hydrogen halides (being least for the iodides and for the hydrogen compounds), and probably to between 2 and 5 volts for the three cuprous halides.<sup>36,37</sup> The observed band systems of the Cu halides probably all correspond to electronic excitation energies lying between 2.4 and 3.1 volts;<sup>42</sup> for the five  $\text{CuI}$  systems the figures are 2.44, 2.68, 2.70, 2.83, and 2.96 volts. The complete absence of ultraviolet band spectra in the Cu halides, and of *all* electronic band spectra in the other halides mentioned, can both, then, be accounted for by the suggestion above in regard to instability of energized molecules.<sup>43</sup>

<sup>40</sup> There appears to be no record whatever in the literature of electronic band spectra for these compounds, in spite of much investigation.

<sup>41</sup> In the case of non-polar compounds such as  $\text{H}_2$ ,  $\text{N}_2$ , and  $\text{I}_2$  it is, however, of course well known that the molecule can possess electronic energy greatly in excess of the heat of dissociation, and can lose this excess energy in band spectrum emission.

<sup>42</sup> This is definitely shown for  $\text{CuI}$  by the preceding analysis, and is also probably true for  $\text{CuBr}$  and  $\text{CuCl}$ .

<sup>43</sup> A possible alternative explanation of the absence of observed band spectra in the compounds mentioned is that they lie wholly in or below the Schumann region. It seems unlikely, however, that this would be consistently true for all members of the class, and that, in addition, no jumps between higher levels would occur giving rise to bands in the visible or ordinary ultraviolet. Also, in recent unpublished work of Dr. L. A. Turner on a mixture of  $\text{H}_2$  and  $\text{I}_2$ , no bands attributable to  $\text{HI}$  were found in the Schumann region. The occurrence in positive rays of such ions as  $(\text{HCl})^+$ ,  $(\text{NaI})^+$ ,  $(\text{HgI}_2)^+$ , etc., suggests

If MX molecules are unable, on account of the absence of an easily excited electron in the ion  $M^+$ , to give electronic band spectra, one would naturally expect the same to be true of  $MeX_2$  molecules, where Me is one of the alkaline earth metals; for the  $Me^{++}$  ion, like the  $M^+$  ion, contains no easily excited electron.<sup>43</sup> As a matter of fact, all the members of this group give band spectra, in the visible and near ultraviolet, with ease; the fact that many of these can be obtained in the Bunsen flame shows that the electronic energy of the emitting molecule is relatively small, the band emission being in all probability accompanied by a return to the normal state of the molecule. These facts obtain a simple explanation in harmony with preceding considerations if one attributes these bands to compounds  $Me^+X^-$  present in small amounts. Such compounds contain one unused valence electron which should be very easily excitable, much like the single valence electron in an M atom. The excitation of MeX spectra by adding  $MeX_2$  to a flame would then be completely analogous to the excitation of M spectra by the addition of MX to a flame (e.g., the excitation of the sodium D lines by adding NaCl to a flame). There is little evidence for compounds of the type MeX in the solid state,<sup>44</sup> but their existence in the vapor state is to be expected, in small amounts in equilibrium with  $MeX_2$  and Me molecules. Such molecules would considerably resemble BO and CN (also SiN); all are "odd molecules" containing a single unused and presumably easily excited valence electron; it may be recalled that in a previous paper<sup>33</sup> considerable evidence was presented for the existence of an analogy between BO and CN and the Na atom. The structure of the spectra of the alkaline earth halides appears to be in agreement with the suggestion that they are due to diatomic molecules, although further investigation is needed. Also, these spectra are characterized by electronic doublets whose separation is of the same order of magnitude as, and which may well be analogous to, those of the spark spectra of the corresponding alkaline earth metals and of the arc spectra of the adjacent alkali metals.<sup>45</sup>

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of course, that these should give electronic band spectra, but it should be remembered that a molecule which has completely lost an electron may be stable even if the same molecule with this electron in a highly excited state is unstable.

<sup>44</sup> But cf. refs. given in J. W. Mellor's "Treatise on Inorganic and Theoretical Chemistry," Vol. III, p. 713; also cf. stability calculations by H. G. Grimm and K. F. Herzfeld, *Zeits. f. Phys.* 19, 141, 1923.

<sup>45</sup> The spectra of the alkaline earth halides contain each apparently two or more band-systems. The spectra of the chlorides, bromides, and iodides of Ca, Sr, and Ba are closely homologous, as was shown by Olmsted (C. M. Olmsted, Dissertation Bonn, 1906; *Zeits. wiss. Phot.* 4, 255-333, 1906). In each case Olmsted investigated particularly one complex system, of homologous structure and similar position for all these



The occurrence of MH,  $M_2$ , and similar spectra is not in contradiction with the preceding considerations, which deal with molecules of a polar type; for the types MH and  $M_2$  are probably analogous to the non-polar molecule  $H_2$  or are loose compounds whose electrons are bound in orbits which do not differ radically from those of the same electrons in the unshared atoms, so that these electrons are capable of being excited, with varying degrees of ease, without causing the molecule to become highly unstable.<sup>41,46</sup> The characteristic emission of band spectra by molecules of the supposedly polar type  $Me^{++}O^-$  is less readily explained, but may be ascribed to an approach to the non-polar type by reason of the expected very marked deformation of the  $O^-$  by the  $Me^{++}$  ion; or, the emission of the bands may be due to a form of the oxide molecule which may be written  $Me^+O^-$ . The band spectra of the halides of Zn, Cd, and Hg probably resemble those of the alkaline earth halides, but the less polar character of the compounds, especially those of Hg, favors the existence of  $MeX_2$  in addition to  $MeX$  bands.<sup>43</sup> Further study is being made of the points touched on above.

JEFFERSON PHYSICAL LABORATORY,  
HARVARD UNIVERSITY,  
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halides. These bands appear to be rather similar to the  $CuX$  bands, except that the shift of the intensity maximum, in successive sequences on either side of the intense band-group which is presumably  $\Delta n=0$ , away from the first head of the sequence, is here much more rapid. Assuming  $n'=0$ ,  $n''=0$  for the most intense band, the bands for each compound can be expressed by quantum theory formulas of substantially the usual type:  $\nu = \nu^e + (a'n' - b'n'^2) - (a''n'' + b''n''^2)$ . Here  $\nu^e = A_1, A_2, B_1$ , or  $B_2$ , constituting an electronic multiplet. There is a major doublet separation  $B-A$ , which increases with the atomic weight of the metal and of the halogen and is of the same order of magnitude as that of the  $2p$  terms for the corresponding  $Me^+$  or  $M$  spectrum, and a minor doublet separation  $A_2-A_1=B_2-B_1$ , which decreases with increasing atomic weight of the metal or halogen. It may be recalled that similar double doublets appear in the  $\alpha$  bands of  $BO$ , the  $\gamma$  bands of  $NO$ , etc. The coefficients  $a'$  and  $a''$ , representing molecular vibration frequencies, are comparable with those of the  $Cu$  halides, and decrease, as might be expected, with increasing atomic weight of  $Me$  and of  $X$ . The positive sign of the coefficient of  $n'^2$  (which it seems impossible to avoid by any other reasonable assignment of vibrational quantum numbers) is not contrary to theory, although it differentiates these bands from all others hitherto analyzed.

<sup>46</sup> For further discussion of hydride bands, see R. S. Mulliken, *Phys. Rev.* **25**, 509, 1925. In  $CuH$ , and, as suggested to the writer by Dr. W. W. Watson, in  $MeH$ , it may be that the first valence electron is engaged in a non-polar bond with the  $H$  electron, while the second behaves as in  $CuX$  and  $MeX$ .

## SHORT-LENGTH TUNGSTEN ARC CHARACTERISTICS

BY S. H. ANDERSON AND G. G. KRETCHMAR

## ABSTRACT

The method used was a dynamical one. Oscillograms were taken giving the current through the arc and the p.d. across the electrodes (4 mm in diam.) as the latter were uniformly separated. This was accomplished by connecting the cam which separated the electrodes directly to the shaft of the oscillograph drum so that the exposure on the film was made while the arc gap was being lengthened. From the measurements of the oscillograms, curves are plotted giving p.d. as a function of current for constant gap length of from 0.005 mm to 0.4 mm, also curves giving p.d. against gap length for different constant current values from 2 to 12 amp. The intercepts of these latter curves on the voltage axis give the "minimal length" characteristic. It is found that (1) for an arc length 0.4 mm, and for shorter gaps where the current is 4 amp. or more, the characteristics are expressed by Nottingham's equation,  $E = A + B/i^n$  where  $n = 1.49$ ; (2) the value of  $n$  for tungsten fits roughly the linear relation of  $n$  to the absolute temperature of the boiling point of the anode material, suggested by Steinmetz; (3) the minimal length characteristic is expressed by  $E = 13.2 + 1.05/(i - 1.75)$ , which makes it possible to compute the constants of an ignition or relay circuit so as to eliminate sparking between tungsten contact points.

## I. INTRODUCTION

THERE has been renewed interest recently in the investigation of the characteristics of electric arcs for two reasons. (1) Information regarding the processes of ionization and values of ionizing potentials have become available so that a more detailed theory of the arc is possible; (2) a knowledge of the characteristics of arcs between metallic contact points is necessary in order to calculate the current potential-difference relations which occur upon opening circuits, such as the primary of an induction coil or an ignition circuit or a relay. K. T. Compton<sup>1</sup> has fully discussed the theory of the electric arc. Nottingham<sup>2</sup> has investigated the characteristics of a number of metallic arcs (copper in particular) and has extended the empirical equation of Ayrton. H. E. Ives<sup>3</sup> has shown the importance of the "minimal length" characteristics of arcs in computing the current potential-difference relations occurring in the discharge as contact points are opened, and has determined these characteristics for gold and platinum. Of all materials used for contact points tungsten is

<sup>1</sup> K. T. Compton, *Phys. Rev.* **21**, 266 (1923).

<sup>2</sup> Nottingham, *J. Am. Inst. Elec. Eng.* **42**, 12 (1923).

<sup>3</sup> H. E. Ives, *J. Franklin Inst.* **198**, 4 (1924).

the most common, and apparently the most satisfactory yet found. So it is highly important to have information of the characteristics of arcs between tungsten electrodes.

## II. METHOD AND EXPERIMENTAL ARRANGEMENT

The method used was a dynamical one. By means of an oscillograph a record was obtained of the current and the potential difference across tungsten contact points as they were uniformly separated. Fig. 1 shows some of the details of this method. An interrupter housing from a Bosch automobile ignition system was mounted on the frame of the oscillograph so that the cam operating the interrupter lever *L* could be directly con-

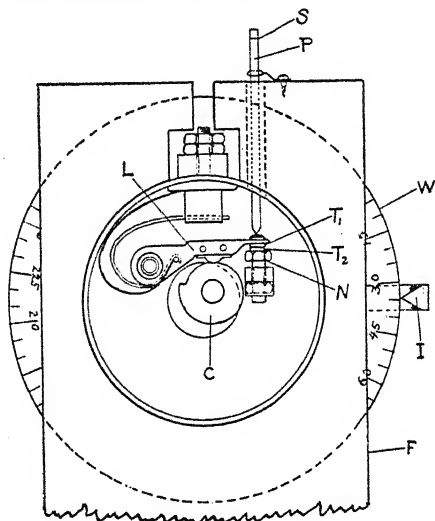


Fig. 1. Arrangement used to separate the tungsten contacts at a uniform rate.

nected to the shaft of the oscillograph drum. The cam *C* was made specially for this work. It was cut in the form of an Archimedean spiral so that for each revolution the contact points opened once. In operation the cam rotated against the fiber friction block of the interrupter lever, thus separating the contact points *T*<sub>1</sub>, *T*<sub>2</sub> and producing a gap which could be predetermined from the form of the cam and the angular position. By means of a screw *N* and lock nuts the interrupter lever could be adjusted to secure proper bearing against the cam. The contact points were 4 mm in diameter, with the contact surfaces flat and carefully polished. Before each oscillogram was taken the surfaces were renewed.

The maximum separation produced was about 0.5 mm and was produced by a rotation of 225° after the initial separation, or in other words, the curves on the oscillogram were distributed over 225/360ths of the

film length. The circular scale  $W$  marked in degrees was attached to the drive pulley on the shaft to give the angular position of the cam while making the calibration. The opening of the contact points was indicated by the motion of the pin  $P$  which rested on the interrupter lever just above  $T_1$ . The movement of  $P$  was read by a micrometer microscope.

Fig. 2 is a diagram of the electric circuits. The current through the arc was recorded on the oscillogram by means of a standard vibrator  $V_1$  used in connection with the usual external shunt arrangement for current measurement. Three shunts were provided, each allowing a deflection of about 6 cm on the film for its rated capacity. The capacities were 5, 10, and 15 amp. respectively.

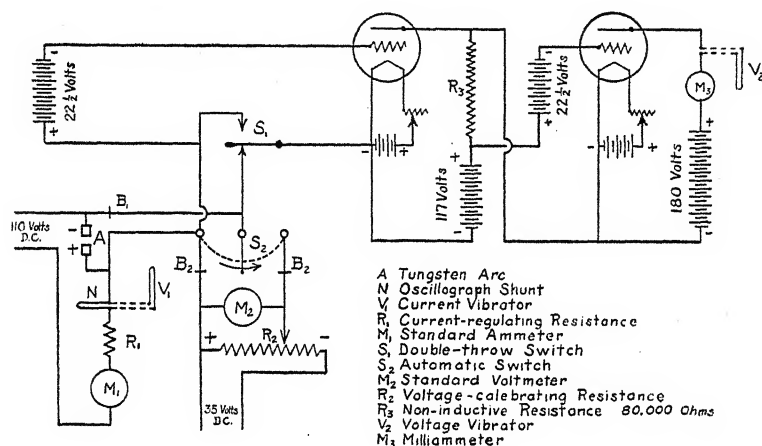


Fig. 2. Diagram of electric circuits

The voltage curve was taken simultaneously with the current on the same oscillogram, by means of a high sensitivity vibrator  $V_2$  and a thermionic tube relay. The thermionic tube arrangement was used in order to give an electrostatic measurement of voltage, so that no current would be diverted from the arc for energizing the voltage vibrator. It consisted of a U.V.201A tube in combination with a Western Electric V.T.2. These were resistance coupled, and the resistance as well as the grid and plate voltages of the tubes were adjusted by trial, so as to give very little deflection for the first 10 volts, and to spread the voltage range from 10 to 30 volts over as great a distance on the film as possible. The values of resistance and voltage used are shown on the diagram.

Oxidation of the tungsten was reduced to a minimum by allowing the current to flow through the arc for about one-half second only, while the exposure was being taken. This was accomplished by means of an auto-

matic switch  $S_2$  which was connected across the arc terminals and was opened simultaneously with the shutter by means of an electromagnetic arrangement. A hand-operated switch (not shown in the diagram) was also connected across the arc terminals, and this was closed, shorting the tungsten contacts again immediately after pulling the string which opened the shutter of the oscillograph. The interval between the opening of the automatic switch and the closing of the hand switch was equivalent to about 3 revolutions of the cam and film drum, as the speed of the drum was about 400 r.p.m. throughout the tests.

The current for the arc was taken from a 110 volt storage battery and adjusted to the proper value by means of the usual regulating resistance in series. The external voltage was maintained at 110 volts throughout the tests. The oscillograph motor and field coils were supplied with 110 volts d.c. from the laboratory motor-generator set.

### III. CALIBRATION AND OPERATION

Before making any oscillograms, accurate calibrations of the current vibrator and external shunts were made. This was done by sending the current through a standard ammeter in series with a regulating resistance and the shunt undergoing calibration. The deflection produced by the oscillograph vibrator on the ground glass was then carefully marked for a series of current values through the shunt, taking from three to five readings for each shunt. The deflections were then carefully measured and the resulting current-deflection curve was drawn as a calibration curve for the shunt. This was checked by the straight portions of the current curves on the final arc oscillograms.

The standard ammeter was checked with a potentiometer and standard cell, and was found to be correct within from  $1/4$  to  $1/2$  percent over the range used.

It was early apparent that the factors which would limit the accuracy of the work were (1) the measurement of the very small arc lengths, and (2) the oxidation of the tungsten contacts. The tungsten points were always carefully adjusted so that their flat surfaces made a close well-fitting contact. Each renewal of tungsten points made necessary a new calibration of the cam setting. The cam was set to open at the same point for each of the films. The calibrations were made by reading the gap width for each  $15^\circ$  for the first  $75^\circ$ , and then for each  $30^\circ$  up to the maximum value of the cam lift at  $225^\circ$ . This work was always carefully done in duplicate and the curves always showed a good agreement, the variation being less than .01 mm between the two sets of readings. To make sure that oxide was absent, new tungsten contacts were installed for

each value of arc current used, except in a few cases where the same contacts were used the second time when a small current had been used at first which did not appreciably oxidize the tungsten.

The voltage calibration data were obtained by running calibration oscillograms. Because of the possibility of variation of the high voltage dry batteries used for the plates of the tubes, it was thought best to take these before, after, and during the operation of taking the arc oscillograms. This was accomplished easily by a special system of wiring which is shown in Fig. 2. When running a calibration oscillogram the arc was disconnected at  $B_1$ , and the automatic switch connected to the potentiometer resistance  $R_2$  through the connections  $B_2$ . The standard laboratory voltmeter was connected across the potentiometer resistance at  $M_2$ . Each calibration line was obtained by setting the automatic switch in the open position, and adjusting the resistance  $R_2$  until the meter  $M_2$  indicated the voltage desired. The oscillograph shutter was then opened, closing the circuit through the automatic switch at the same time, thus throwing the voltage indicated on  $M_2$  against the constant negative grid bias of the first tube, and giving a line on the film corresponding to the applied voltage. The switch  $S_1$  was kept closed on the side of the  $22\frac{1}{2}$  volt negative grid bias all the time of making the calibration, except during the time of taking the exposure, thus keeping the continuous output of the tubes down to a safe small value. Table I shows the average measurements taken from four calibration oscillograms.

TABLE I

*Average measurements for voltage calibration curve.*  
Taken from oscillograms Nos. 4, 8, 11, 14 at positions  $10^\circ$  to  $155^\circ$

Voltage	$10^\circ$	$32^\circ$	$81^\circ$	$120^\circ$	$155^\circ$
0	0				
10	.10	.11			
12	.43	.43			
13	.73	.73			
14	1.07	1.07			
15	1.31	1.31			
17	1.69	1.69	1.69	1.67	1.67
19	2.34	2.33	2.33		
20	3.07	3.07	3.06	3.05	3.04
21	3.54	3.55	3.53	3.53	
23	4.16	4.15	4.14	4.12	4.11
25		4.54	4.52	4.50	4.48
26		4.74	4.72	4.72	4.70
30		5.36	5.34	5.32	5.30

The data of Table I show the effect of the space charge. The space charge seemed to exercise a reservoir effect giving slightly augmented values of the tube output until the excess electrons were used up, which occurred, for a speed of 400 r.p.m., after the drum had traveled  $150^\circ$ .

The effect was observable only for the larger voltage values used, appearing as a slight increase in the amplitude of the calibration line for voltages above 20 volts, and on the first part of the film record. The effect was taken into account on the calibration curve.

The operation of making an arc film was as follows. (1) The new tungsten points were properly adjusted and the cam setting calibrated. (2) The automatic switch was closed, thus short-circuiting the arc. (3) The oscillograph arc light was started and the adjustment of the vibrators tested. (4) The oscillograph shutter was set. (5) The thermionic tube filament currents were turned on and adjusted to the proper values by means of the ammeters in the filament circuits. (6) The film drum was attached and the motor started. (7) Exposure was made for the zero lines. (8) The current through the arc was adjusted to the value desired

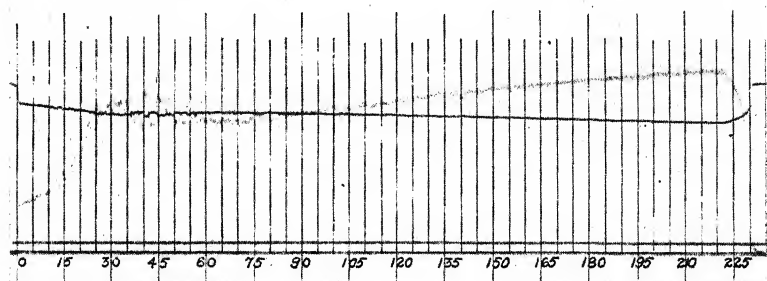


Fig. 3. Typical oscillogram and scale.

and the value recorded as observed on the standard meter  $M_1$ . (9) Making sure that the arc light was burning satisfactorily and that the tube filaments had remained constant, the shutter string was pulled making the exposure and then the hand-operated switch was closed. (10) The circuits were all opened and the film developed.

A typical oscillogram is shown in Fig. 3 which shows a film taken with the 5-ampere shunt and an initial current of 3.8 amp. The ruled scale shows the form used under the oscillograms during measurements.

#### IV. RESULTS

1. *Arc characteristics.* In Fig. 4 are shown the arc characteristics obtained by plotting the potential difference against current. The lowest curve is the "minimal length" characteristic, obtained as described below. From this set of curves potential differences corresponding to different gap lengths for a constant current value were read off and plotted in



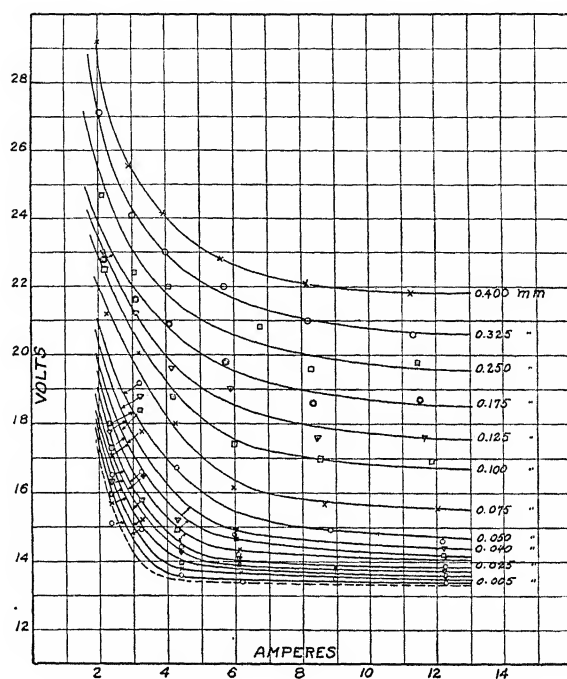


Fig. 4. Arc characteristics for constant length.

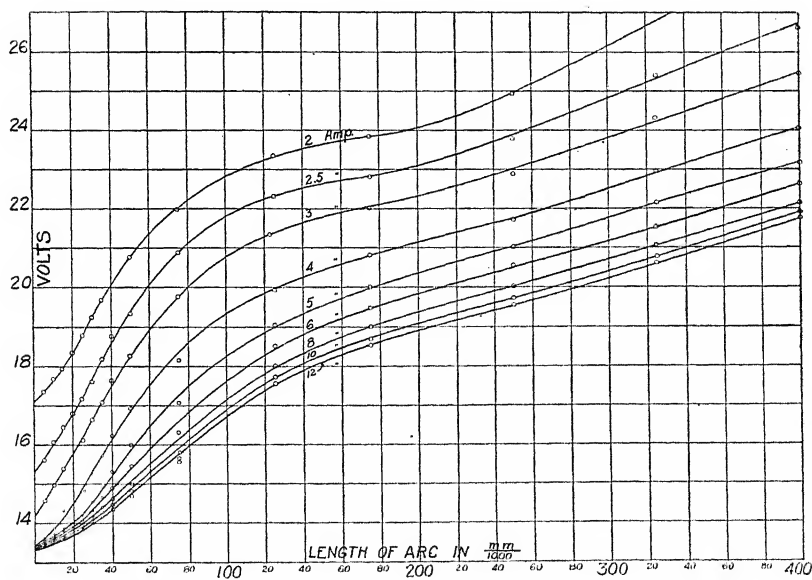


Fig. 5. Characteristics for constant current.



Fig. 5. It is interesting to note that while the general form of the curves in this set is similar to that found by other observers (for example Nottingham), the lower portion shows an upward inflection. This method has made it possible to obtain data for smaller gap lengths than previously reported, so that the intercepts of these curves on the voltage axis are given with considerable certainty. These intercepts, which are potential differences corresponding to currents of 2, 4, 6, 8, and 10 amp. respectively for zero arc length, were read off and plotted in Fig. 4 as the dashed line. *This is the "minimal length" characteristic for the arc between tungsten electrodes.* The convergence of the curves of Fig. 4 to the dashed curve is in agreement with the observation of Ives<sup>3</sup> for gold and platinum, that "the minimal length characteristic . . . is obviously a member of the family of finite length characteristics."

2. *Equation for arc characteristic.* Nottingham<sup>2</sup> has proposed the following empirical equation for arc characteristics

$$E = A + B/i^n$$

in which  $E$  is the potential difference across the arc,  $i$  the current,  $A$  and  $B$  constants for a given arc length and electrode material, and  $n$  a constant characteristic of the material but independent of the length. This may be considered a more general form of the equation found by Mrs. Ayrton<sup>4</sup> to hold for carbon arcs. The constants of this equation can be evaluated only by a semigraphical method.<sup>5</sup> Values of  $A$  were found for ten gap lengths from 0.4 mm to 0.03 mm, and then  $\log (E - A)$  plotted against  $\log i$  (Fig. 6). For two larger gaps, 0.4 mm and 0.325 mm, the points are uniformly distributed about a straight line and the two lines are nearly parallel. So we may conclude that for gaps of the order of 0.4 mm (and probably larger) Nottingham's equation holds for the tungsten arc in air. The slopes of these lines gives the value of  $n$ . The average for the two upper lines is 1.487. For gaps smaller than 0.325 mm the upper points depart considerably from a straight line, but the lower points ( $i > 4$  amperes) lie very close to a straight line parallel to those of the larger gap. Using the straight portion of the first five logarithmic graphs, the average value is nearly the same, 1.48. An inspection of Fig. 4 suggests that, while the lower curves differ in form from the upper, the whole set is one family of curves and it should be possible to find an equation which would hold for all. However, an attempt to do this will be

<sup>4</sup> Hertha Ayrton, *The Electric Arc*, The Electrician Printing and Publishing Co., London, 1902.

<sup>5</sup> Lipka, *Graphical and Mechanical Computation*, John Wiley & Sons, New York, 1918, p. 140.

deferred until a redetermination of the characteristics is made with greater precision. In the present work the possible error in the potential difference is  $\pm 1.0$  volt which makes the exact form of the curves rather uncertain.

3. *Equation for minimal length characteristic.* Ives found that the minimal length characteristics for carbon, gold, and platinum can be satisfactorily represented by the following equation

$$E = a + \gamma / (i - c).$$

Furthermore, this equation is well adapted to the calculations involved in determining the constants of a circuit such that the arcing is a mini-

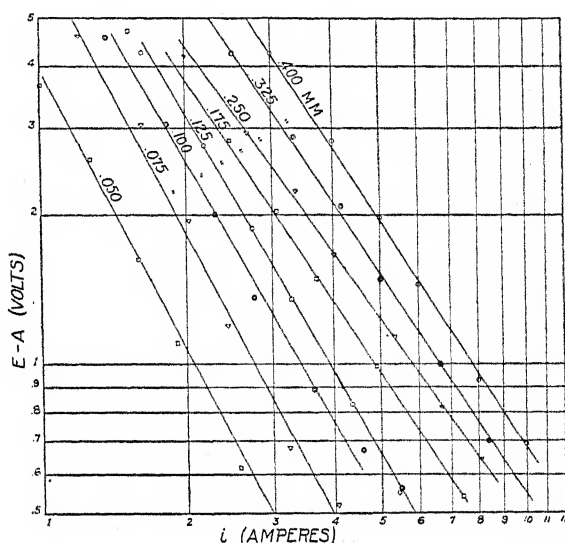


Fig. 6.  $\log (E-A)$  as a function of  $\log i$ .

imum at the opening of contacts. Within the limits of experimental error this equation will also serve for the tungsten minimal length characteristic, the equation after determining the constants being given by

$$E = 13.2 + 1.05 / (i - 1.75).$$

From this it is seen that the arc will not persist when the current is 1.75 amperes or less, no matter what potential difference is applied at the electrodes. This agrees with observations made for small current values. No oscillograms of a persisting arc were obtained when the initial current was less than the above value.

4. *Relation of  $n$  to the temperature of the boiling point of the electrode metal.* Steinmetz<sup>6</sup> suggested that the temperature of the vapor in the arc is a constant depending upon the boiling point or sublimation point of the material of the anode. Nottingham, following out this suggestion, proposes that the constant  $n$  of his equation is a linear function of the absolute temperature of the boiling point or sublimation point of the material of the anode, and obtains a table of values that fit a straight line very well. However, for the anode of aluminum, cadmium, and zinc respectively he uses the boiling point of the metallic oxide rather than

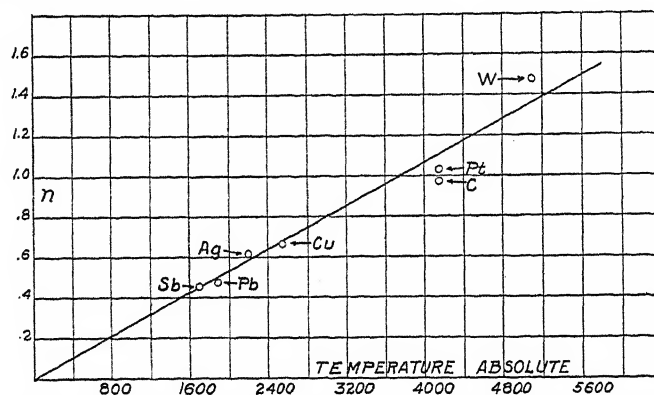


Fig. 7. Constant  $n$  of Nottingham's equation as a function of boiling temperature.

the metal. We have extended Nottingham's graph by two points, computing  $n$  for platinum from Ives curves<sup>3</sup> and  $n$  for tungsten from our own work. This is shown by Table II and Fig. 7.

TABLE II

Cathode	Anode	$n$	Authority	Boiling point	Authority
carbon	antimony	0.460	Nottingham	1710°K	Greenwood 1910
carbon	lead	0.480	"	1883	Van Liempt 1920
carbon	silver	0.624	"	2214	" " "
copper	copper	0.670	"	2562	" " "
copper	carbon	0.985	"	4187	" " "
platinum	platinum	1.15	Ives (Anderson)	4180	Langmuir 1914
tungsten	tungsten	1.487	Anderson & Kretchmar	5100	" "

The temperatures used were taken from Landolt-Bornstein Physikalischen-Chemische Tabellen, Fifth Edition, 1923 (except for platinum and tungsten) and are not quite the same as those given in Nottingham's paper. The questionable materials, aluminum, cadmium, and zinc are omitted from Table II and Fig. 6. Within the limits of experimental

<sup>6</sup> Steinmetz, Radiation, Light and Illumination, McGraw-Hill, New York, p. 140.

error the points fit a straight line. If more precise determinations verify the validity of Nottingham's equation and the linear relation of  $n$  to the absolute temperature of the boiling point of the anode, we shall have a new method of finding the boiling points of metals.

We wish to express our appreciation of the assistance given in this experimental work by the Bosch Magneto Corporation who furnished materials and by Mr. L. F. Curtis, Chief Engineer, who gave valuable advice and suggestions from his experience with ignition circuits. The oscillograph used was kindly loaned by the Department of Electrical Engineering, University of Washington.

DEPARTMENT OF PHYSICS,  
UNIVERSITY OF WASHINGTON,  
SEATTLE, WASHINGTON,  
March 18, 1925.

# THE IONIZATION OF HYDROGEN BY ELECTRON IMPACT AS INTERPRETED BY POSITIVE RAY ANALYSIS\*

BY T. R. HOGNESS AND E. G. LUNN

## ABSTRACT

**Ions produced in hydrogen by electron impact.**—Using an apparatus previously described in which positive ions formed by impact of electrons of definite energy ( $V_1 + V_2$ ) are accelerated and then deflected magnetically around a semi-circle into a Faraday cylinder, the relative numbers of ions of types  $H^+$ ,  $H_2^+$  and  $H_3^+$  were measured as a function of pressure from  $<0.1 \times 10^{-4}$  mm to .006 mm, and also as a function of impact energy ( $V_1 + V_2$ ) to 60 volts. At low pressures only  $H_2^+$  ions are formed; as the pressure is increased the percentage of  $H_3^+$  increases in proportion to the pressure. In the apparatus used, the percentage of  $H^+$  increased with pressure but did not exceed 4 percent, while the percentage of  $H_3^+$  ions reached 60. These results confirm the conclusions of Dempster and Smyth that the primary process in the ionization of hydrogen is the ionization of the molecule without dissociation. The previously measured ionization potential at 16 volts (confirmed in this work) is that for the formation of  $H_2^+$ .  $H_3^+$  also appears at this potential, but as a result of a secondary process. It appears that the  $H_2^+$  ion is readily dissociated by collision and that the  $H^+$  ion formed may unite with the  $H_2$  molecule collided with or with some other molecule to form  $H_3^+$ . The interpretation of ionization potentials reported by other observers is discussed in the light of these results.

**Ions produced in helium containing hydrogen, by electron impact.**—The percentage of  $H^+$  ions found was greater even than the percentage of  $H_2^+$ , while no  $H_3^+$  ions were observed. Evidently the primary ions  $H_2^+$  are readily dissociated by impact with He atoms. Evidence was found for the ions  $HeH^+$  and also for an ion with  $m/e=6$ , perhaps  $HeH_2^+$ .

IN a recently published preliminary report<sup>1</sup> the authors have described the apparatus employed in this investigation and have given the conclusions that could be drawn from the scanty results then available. By changing the experimental procedure and widening the range of experimental conditions employed they have since made a more detailed study of the problem. The results of this study have made untenable the conclusion formerly drawn that in the ionization of hydrogen by electron impact there are two independent primary processes



\* When this paper was first submitted the authors were informed by the editor that an article by H. D. Smyth, "Primary and Secondary Products of Ionization in Hydrogen," was already in press (Phys. Rev. 25, 452, April 1925). Through the kindness of the editor we have had the advantage of reading proof of that article and have accordingly revised the discussion in this paper to give recognition to Smyth's work.

<sup>1</sup> Hogness and Lunn, Proc. Nat. Acad. Sci., 10, 398 (1924).

and have given evidence that Eq. (1) represents the only primary process, the formation of  $H^+$  and  $H_3^+$  being secondary. This is the conclusion drawn by Dempster<sup>2</sup> in a much overlooked and neglected paper from his investigation of the ionization of hydrogen by high-voltage electrons, and also by Smyth.<sup>3</sup>

#### DESCRIPTION OF THE APPARATUS AND METHOD

The apparatus (Fig. 1) is essentially an ionization potential tube so arranged that the products of ionization can be analyzed by Dempster's<sup>4</sup> positive-ray method. The preliminary report of this work gives a detailed description of the apparatus which need not be repeated here. Consideration of the equation  $e/m = 2V_4/H^2r^2$  by means of which

TABLE I  
*Electrometer readings for  $H^+$ ,  $H_2^+$  and  $H_3^+$  peaks, at various pressures.*

Pressure ( $10^{-4}$ mm)	Readings			Percent		
	$H^+$	$H_2^+$	$H_3^+$	$H^+$	$H_2^+$	$H_3^+$
<0.1	0	360	0	0	100	0
	0	241	0	0	100	0
2.0	5	520	1.3	0.9	96.7	2.4
	3	434	0.8	0.7	97.5	1.8
5.4	17	850	35	1.9	94.2	3.9
	17	630	33	2.5	92.6	4.9
	18	900	49	1.9	93.0	5.1
11	8	500	94	1.3	83.1	15.6
	5	320	45	1.3	86.5	12.2
12	7	520	103	1.1	82.6	16.3
	10	512	115	1.6	80.1	18.3
15	15	530	110	2.3	81.0	16.7
22	1(?)	220	69	0.3(?)	75.9	23.8
	33	1000	265	2.5	77.1	20.4
28	28	560	260	3.3	66.1	30.6
	27	560	240	3.3	67.7	29.0
39	61	720	540	4.6	54.5	40.9
	27	520	360	3.0	57.3	39.7
56	40	470	690	3.3	39.2	57.5
	36	460	680	3.1	39.1	57.8
He and $H_2$	153	70	0	68.6	31.4	0

<sup>2</sup> Dempster, Phil. Mag. 31, 438 (1916).

<sup>3</sup> H. D. Smyth, Phys. Rev. 25, 452 (April 1925). See also Proc. Roy. Soc. 102A, 283 (1922); 104A, 121 (1923); 105A, 116 (1924); Nature, 111, 810 (1923); 114, 124 (1924); Phys. Rev. 23, 297 (1924); J. Franklin Inst. 198, 795 (1924).

<sup>4</sup> Dempster, Phys. Rev. 11, 316 (1918).

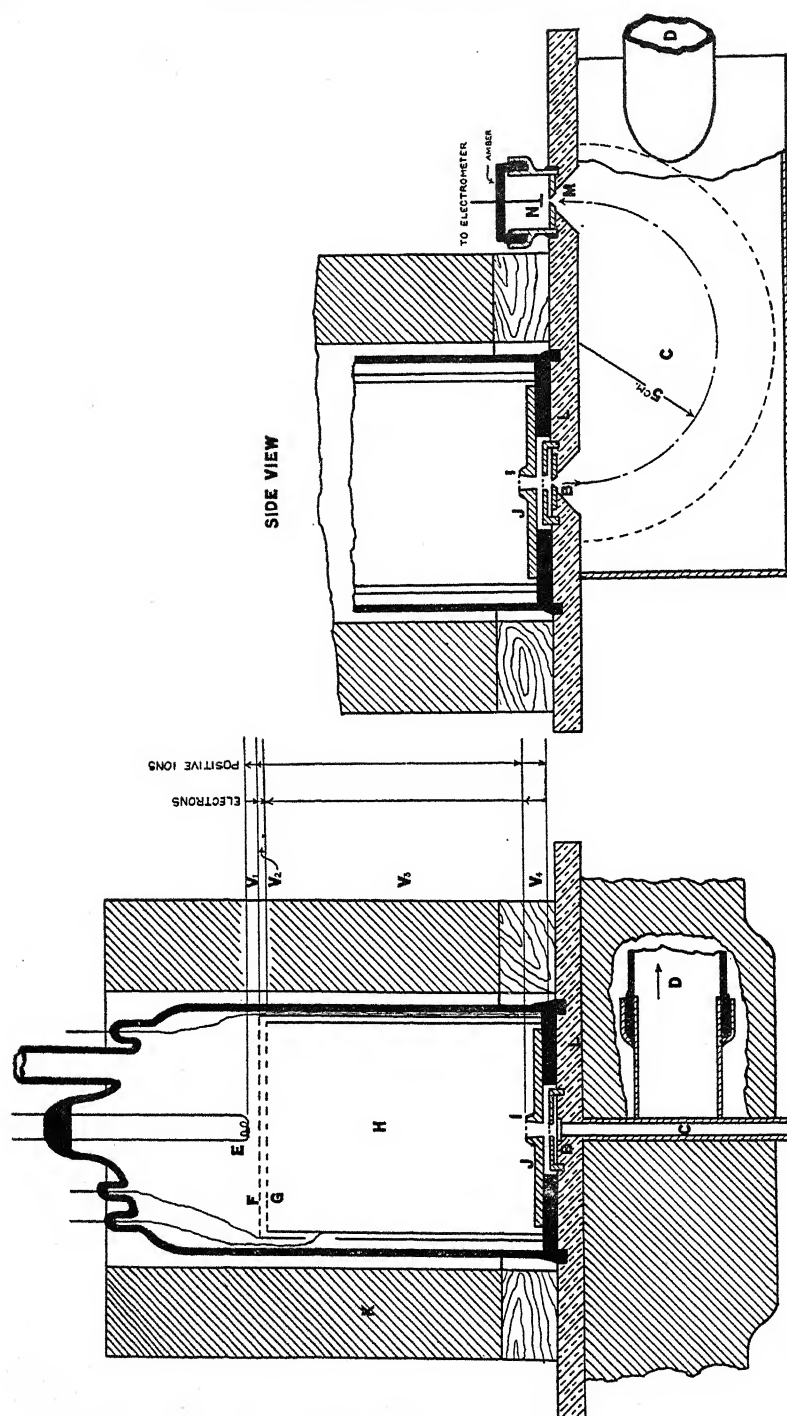


Fig. 1. Apparatus for positive ray analysis of ions.

the specific charges are determined, shows that two experimental procedures are open, (1) that of keeping the magnetic field  $H$  constant and focussing the ion beam by varying the accelerating potential  $V_4$ , and (2) that of varying the magnetic field while  $V_4$  is kept constant. The former procedure was used in searching for new ions and for measuring their specific charges, the latter in measuring the ionic intensities since its use permitted constancy of electrical conditions in the tube and gave consistent and reproducible results.

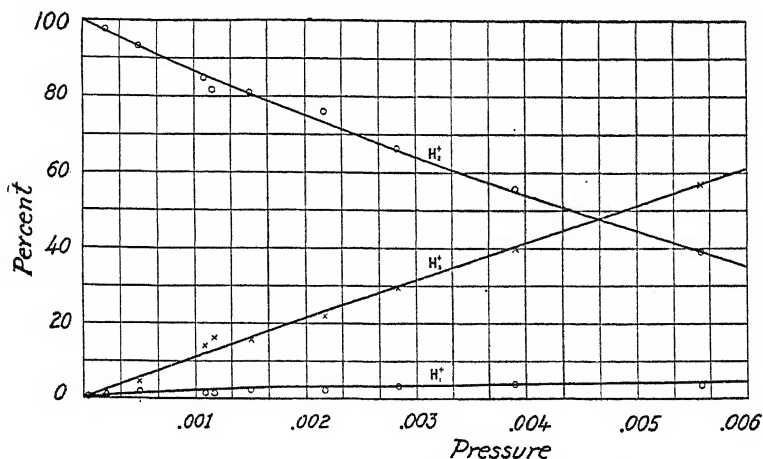


Fig. 2. Percentage of each of ionic species ( $H^+$ ,  $H_2^+$ ,  $H_3^+$ ) as a function of pressure.

Of the present experiments those that seem to throw most light on the problem of interpreting the processes of ionization are the ones on the change of the relative intensities of the ions  $H^+$ ,  $H_2^+$  and  $H_3^+$  with change in pressure. The data from these experiments are recorded in Table I. The electrometer deflections given were obtained with the constant deflection method. The right-hand side of Table I gives the percentage of each ionic species present as measured by the electrometer deflection ratio. The averages of the values for each pressure given in the table are plotted in Fig. 2, in which the pressures are recorded as abscissas and the percentages as ordinates.

It is evident from the table and from Fig. 2 that as the pressure is lowered the percentages of  $H^+$  and  $H_3^+$  decrease in a regular manner and approach zero at zero pressure. This clearly indicates that the formation of  $H_2^+$  is the primary process and that  $H^+$  and  $H_3^+$  are formed from  $H_2^+$  as the result of secondary collisions with gas molecules.  $H_2^+$  is appar-



ently metastable and is disrupted when it collides with a neutral gas molecule in one of two ways



If Eq. (4) represents the sole collision reaction then the formation of  $H_3^+$  would be the result of the tertiary process



Now if  $H_3^+$  were formed only by the reaction (5), in order to account for the fact that the intensity of  $H^+$  was very small at all pressures, it would be necessary to conclude that the proton has a much smaller mean free path than would be predicted from kinetic theory considerations. Hence it seems reasonable to suppose that when  $H_2^+$  ions collide with neutral molecules the reaction taking place in the majority of cases is (3), and that reaction (4) takes place less often.

When the field  $V_3$  for drawing the positive ions from the ionization chamber was increased to such an extent that only those electrons in the upper portion of that chamber had ionizing energy, then the intensity of  $(H^+ + H_3^+)$  increased with respect to that of  $H_2^+$  as might have been expected since the  $H_2^+$  ions formed had greater chance of collision having had a longer average path to traverse. Moreover the ratio of the intensity of  $H^+$  to that of  $H_3^+$  increased considerably. This can be explained by assuming that under these conditions  $H_2^+$  breaks up more often in accordance with reaction (4). This would happen if when the  $H_2^+$  ion acquires sufficient energy before colliding, the  $H^+$  formed by disruption were not trapped by the  $H_2$  molecule to form  $H_3^+$  but passed on into the resolving chamber.

There remains the possibility, however, that  $H_2^+$  is stable and must acquire a definite velocity before a collision would result in disruption into  $H^+$  and  $H$ . To examine this the change in the percentage of  $(H_3^+ + H^+)$  with small variations of  $V_3$  was studied. It was found that as  $V_3$  was gradually lowered from 4.5 volts to 0.1 volt,  $(V_1 + V_2)$  being 48 volts, the percentage of  $(H_3^+ + H^+)$  increased very slightly instead of decreasing as might be expected if energy were required to cause  $H_2^+$  to break up. Although inconclusive, this result seems to indicate that  $H_2^+$  is energetically unstable. This conclusion is in accord with the following, deduced by Sommerfeld on theoretical grounds. "The  $H_2^+$  ion is *unstable energetically*; it can dissociate into  $H$  and  $H^+$ , giving up energy. At the same time it follows from this for the ionization of the  $H_2$  molecule that if this happens in the sense of scheme [Eq. (1)] it requires a greater

ionization potential than if it proceeds according to the scheme [Eq. (2)]. This conclusion is independent of any assumptions about the model of the neutral  $H_2$ , and also remains preserved if we pass from the  $H_2^+$  molecule considered so far to a far more general molecule."<sup>5</sup>

In the experiments plotted in Fig. 2, 48 volts were applied to the impact electrons. The effects of slower speed electrons were investigated at one arbitrarily chosen pressure by obtaining the percentages of the several ions as a function of  $(V_1 + V_2)$  (Fig. 3). The increase in the percentage of  $H_3^+$  as  $(V_1 + V_2)$  was decreased may be explained as due to the characteristics of the discharge tube. The now greater retarding potential  $V_3$  decreased the velocity of those electrons that had penetrated into the lower part of the ionization chamber ( $H$  of Fig. 1) to such an extent that they could not ionize the gas. The  $H_2^+$  ions were then formed at a greater average distance from the gauze  $I$ , and having had a longer

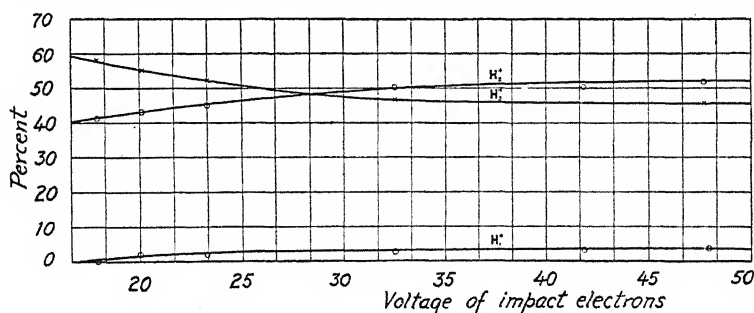


Fig. 3. Variation in relative numbers of  $H^+$ ,  $H_2^+$  and  $H_3^+$  ions with energy of impact electrons.

average path to traverse had greater chance to collide. The curves of Fig. 3 could not be extended below 18 volts with accuracy because of the small intensity of each of the ionic species. Little significance, moreover, can be attached to the  $H^+$  percentage curve at low voltages because of the inaccuracy of measurement of the small  $H^+$  ion current in this region. From these observations of Fig. 3, we conclude that the processes described above are also true for impact electrons of smaller velocities.

Some experiments were made on relative ionic intensities in mixtures of helium with a relatively small amount of hydrogen. It was found that the percentage of  $H^+$  was much greater than in pure hydrogen at any pressure employed (see the last line of Table I). Under these conditions the reactions designated by Eqs. (3) and (5) are much less probable and the  $H_2^+$  on collision with the He atom disrupted to form  $H^+$ .

<sup>5</sup> Sommerfeld, "Atomic Structure and Spectral Lines," 1st Eng. Ed. Appendix 14, page 605.

With mixtures of helium and hydrogen in the tube two particularly interesting intensity peaks of  $m/e=5$  and a less definite one at about  $m/e=6$  were observed repeatedly. A typical run showing these is plotted in Fig. 4. Although the small amount of these ions did not permit of a study of their origin, there is little doubt that the  $m/e=5$  ion is the ion of helium hydride,  $\text{HeH}^+$ , while the other may be  $\text{HeH}_2^+$ .

#### THE IONIZATION POTENTIAL

To determine the ionization potential for the formation of  $\text{H}_2^+$ ,  $V_4$  was set to give the peak of the  $\text{H}_2^+$  intensity curve and with the magnetic

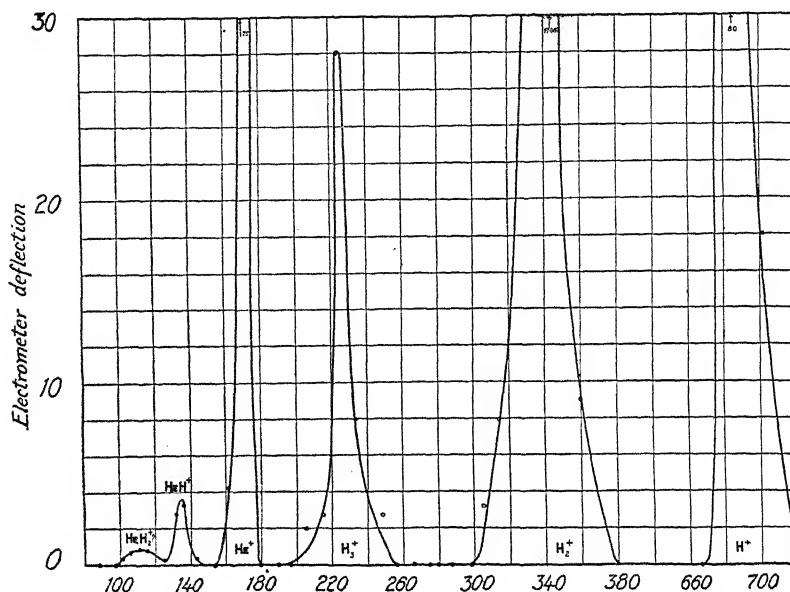


Fig. 4. Peaks obtained with mixture of He and  $\text{H}_2$ .

field, the filament current,  $V_1$  and  $V_3$  all held constant, the electrometer current was noted as  $V_2$  was decreased in steps of 0.3 volt. When the rate of deflection of the electrometer was plotted against  $V_1 + V_2$ , curves like that of Fig. 5 (labelled  $\text{H}_2^+$ ) were obtained. The point at which each curve cut the zero ordinate was taken as the approximate (uncorrected) value of the ionization potential. Then by setting  $V_1$  and  $V_2$  immediately above and below this, and observing the electrometer deflection over a long period of time, a more accurate value was obtained.

To obtain the necessary correction to be applied because of the initial velocity of the electrons, the potential drop along the filament, and contact differences of potential, and to take into account the sensitivity of

the apparatus, helium was introduced into the tube and the ionization potential curve for  $\text{He}^+$  obtained in a manner analogous to that described for  $\text{H}_2^+$ . (See Fig. 5,  $\text{He}^+$ .) 24.5 volts was taken as its true ionization potential. In order that the corrections thus found should have any significance it was necessary to choose the hydrogen and helium pressures such that (1) the "saturation" intensities of  $\text{He}^+$  and  $\text{H}_2^+$  be the same, and (2) the ionization potential curves for helium and for hydrogen be of approximately the same shape. This choice of pressures was made as follows. It was found that 50-60 volts was above the "saturation" voltage. The intensity of the  $\text{He}^+$  line in the calibration run when  $V_1 + V_2$  was about 60 volts was therefore noted, the helium then pumped out, and hydrogen introduced at such a pressure as gave a  $\text{H}_2^+$  line of this same intensity. The smaller figure of Fig. 5 shows the appearance of the ionization potential curves for the  $\text{He}^+$  and  $\text{H}_2^+$  when the respective pressures were so chosen. The two curves are evidently almost superposable.

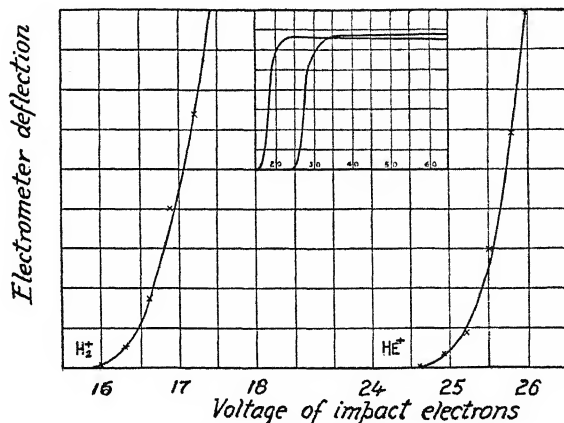


Fig. 5. Variation of intensity of peaks  $\text{H}_2^+$  and  $\text{He}^+$  with energy of impact electrons.

The corrected values for the ionization potential of hydrogen found in successive runs are: 16.3, 16.5, 15.7, 15.8, 16.1, 15.9, 15.8, 15.8. The average value is 16.0.

To show that  $\text{H}_3^+$  and  $\text{H}_2^+$  appear at the same ionization potential, the pressure was so regulated that the  $\text{H}_3^+$  and  $\text{H}_2^+$  lines were of equal intensity and the potentials for the formation of the two ions compared. Under these conditions the two potentials were identical, but at lower pressures where  $\text{H}_2^+$  predominated,  $\text{H}_3^+$  and  $\text{H}^+$  were not detected at as low voltages as was  $\text{H}_2^+$ .

The several lines of investigation presented above unite then in giving evidence that, in the ionization of hydrogen by electron impact, the

primary process of ionization is the detachment of an electron from a molecule ( $H_2 = H_2^+ + e$ ) and that the  $H_2^+$  thus formed is probably energetically unstable and can break up on collision to give  $H^+$  (and  $H$ ). The evidence that the formation of  $H^+$  is the result of a secondary process may be briefly summarized. (1) At very low pressures no  $H^+$  was found; (2)  $H^+$  was never found with impact electrons having a velocity lower than the minimum necessary for the production of  $H_2^+$ ; and (3) with mixtures of helium and hydrogen large amounts of  $H^+$  were found.

The following then are the conditions for producing in a discharge tube each of the different ions of hydrogen in predominating amounts: For  $H^+$ , large potential difference and the addition of some inert gas such as helium; for  $H_2^+$ , low pressures; for  $H_3^+$ , higher pressure and small potential difference.

#### DISCUSSION

It is of interest to note that the above results and the main conclusions derived therefrom are exactly in accord with the following conclusion of Dempster<sup>2</sup> who used 800 volt electrons in his experiments: "... electrons ionize only by detaching a single electron from the molecule, and are not able to dissociate the molecule into atoms." Graphical analysis of his intensity ratios shows also that at zero (extrapolated) pressure no  $H^+$  or  $H_3^+$  would be formed. The present conclusions also agree in the main with those of Smyth,<sup>3</sup> differing therefrom only in detail as to the secondary process. He concludes that the formation of  $H_3^+$  is a tertiary process while we believe it to be largely a secondary one (Eq. 3). Smyth's Fig. 6 shows in a striking manner the increase of  $H_3^+/H^+$  with decrease of  $V_3$ . This we believe gives support to our view. In discussing the stability of  $H_2^+$ , Smyth maintains that if that ion were stable with respect to  $H^+$  and  $H$ , the additional energy necessary for its disruption would have to be supplied by the impacting electron; but this energy could also be supplied by the kinetic energy of the  $H_2^+$  acquired from the electrical field. The possibility may be pointed out here that, contrary to the conclusions drawn from theoretical considerations,  $H_2^+$  may be stable with respect to  $H^+$  and  $H$ , and yet be unstable with respect to  $H_3^+$ , i.e. the reaction (3) may take place with evolution of energy while that of equation (5) may not. There does not seem to be as yet sufficient experimental evidence to test this possibility.

The recently reported spectroscopic investigations of Richardson and Tanaka<sup>4</sup> on low voltage arcs in hydrogen lead them also to conclude that the primary process of ionization is the formation of  $H_2^+$ .

<sup>4</sup> Richardson and Tanaka, Proc. Roy. Soc. 106A, 663 (1924).

It may be well to discuss the bearing of the results of the positive ray studies on critical potential measurements. Table II gives the measurements of several observers on the critical potentials which they

TABLE II  
*Ionization potentials of hydrogen.*

Observers	Values in volts				
Davis and Goucher <sup>7</sup>	11		15.8		
Bishop <sup>8</sup>	11		15.7		
Found <sup>9</sup>			15.8		
Compton and Olmstead <sup>10</sup>	10.8		15.9		
Krüger <sup>11</sup>	11.5		16.4	29.7	
Boucher <sup>12</sup>		13.6	15.6		
Foote and Mohler <sup>13</sup>			16.0		
Mohler, Foote and Kurth <sup>14</sup>			16.0		
Olmstead <sup>15</sup>	11.5	13.6	16.0		
Horton and Davies <sup>16</sup>		13.5	15.9	22.8	29.4
Mackay <sup>17</sup>			15.8		
Olson and Glockler <sup>18</sup>			16.7		
Olmstead and Compton <sup>19</sup> (2800°C)		13.5			
Smyth <sup>3</sup>			16.0		
	Mean		16.0		

ascribe to ionization of hydrogen. All are in agreement concerning the existence of an ionization potential at about 16 volts, but all except Smyth have interpreted this potential as that at which ionization plus dissociation (Eq. 2) takes place. This interpretation is obviously no longer tenable. The 13.5 volt point observed has been ascribed to ionization of the hydrogen atom, the atomic hydrogen presumably being formed by thermal dissociation or by collision of an excited hydrogen molecule with an unexcited one (see below). The potential at about 11 volts which has been interpreted by some observers as that for the process  $H_2 = H_2^+ + e$ , is probably due to excitation, or, as suggested by Horton and Davies,<sup>20</sup> to the ionization of mercury vapor. A new interpretation must

<sup>7</sup> Davis and Goucher, Phys. Rev. **10**, 101 (1917).

<sup>8</sup> Bishop, Phys. Rev. **10**, 244 (1917).

<sup>9</sup> Found, Phys. Rev. **16**, 41 (1920).

<sup>10</sup> Compton and Olmstead, Phys. Rev. **17**, 45 (1921).

<sup>11</sup> Krüger, Ann. der Phys. **64**, 288 (1921).

<sup>12</sup> Boucher, Phys. Rev. **19**, 189 (1922).

<sup>13</sup> Foote and Mohler, Origin of Spectra, p. 68.

<sup>14</sup> Mohler, Foote and Kurth, Phys. Rev. **19**, 414 (1922).

<sup>15</sup> Olmstead, Phys. Rev. **20**, 613 (1922).

<sup>16</sup> Horton and Davies, Phil. Mag. **46**, 872 (1923).

<sup>17</sup> Mackay, Phil. Mag. **46**, 828 (1923); Phys. Rev. **24**, 319 (1924).

<sup>18</sup> Olson and Glockler, Proc. Nat. Acad. Sci. **9**, 122 (1923).

<sup>19</sup> Olmstead and Compton, Phys. Rev. **22**, 559 (1923).

<sup>20</sup> Horton and Davies, loc. cit.<sup>16</sup> In their helium studies they were able to detect mercury vapor spectroscopically in spite of precautions taken to prevent its entrance.

also be sought for the 22.8 volts potential of Horton and Davies, and for the 29.4 and 29.7 points of these observers and of Krüger respectively. The first was ascribed to molecular ionization, the second to molecular dissociation with ionization of both atoms,  $H_2 = 2 H^+ + 2e$ . If such a process as this last took place the lower curve of Fig. 3 would show an increase in the percentage of  $H^+$  at about 30 volts. Olson and Glockler<sup>18</sup> found nine critical potentials in the interval between 14.86 and 16.68 volts, five of which, in addition to the ionization potential, are each 3.16 volts greater than a resonance potential or ionization potential of atomic hydrogen. They interpret these five critical potentials as measuring the energy necessary to dissociate the molecule and resonate one of its atoms, the 3.16 volts being then the heat of dissociation. The three remaining lines which have no apparent relation to the Lyman series they ascribe to molecular excitation not accompanied by dissociation. Hughes<sup>21</sup> in considering Smyth's earlier work in the light of his own experiments, concluded that excitation by electron impact is often accompanied by dissociation. If this view is accepted the interpretation of Olson and Glockler's work, with the exception of the ionization potential, remains unchanged. Von Keussler,<sup>22</sup> however, concluded from a study of spectral data, including his own, that dissociation is an effect secondary to molecular excitation and occurs if the excited molecule is disturbed, as by collision, before it has time to radiate. Such dissociation by collision results only if the excited molecule has energy in excess of that necessary to dissociate the molecule and produce the excited atom. In view of the present experiments and those of Smyth, it appears that von Keussler's theory is the more logical one. There can be very little difference between an ionized molecule and one in the higher stages of excitation. If dissociation does not accompany ionization it would hardly be expected to accompany excitation. If von Keussler's view is adopted, the interpretation of Olson and Glockler's work follows immediately. The 3.16 volts represents, then, the energy of the excited molecule in excess of the energy of the excited atom. If the excited molecule is energetically unstable with respect to its dissociation products and radiates energy or produces kinetic energy on dissociation, the heat of dissociation must then be less than 3.16 volts. While this excess energy of the excited molecule may not be the same for all stages of excitation, any differences that exist may be small enough to fall within the limits of error of the measurements of Olson and Glockler.

<sup>21</sup> Hughes, *Phil. Mag.* 48, 56 (1924).

<sup>22</sup> Von Keussler, *Zeits. f. Physik*, 14, 19 (1923).



It may be of interest to note that the results of the experiments on mixtures of helium and hydrogen described above point toward an explanation of Merton and Nicholson's<sup>23</sup> experiments on the extension of the Balmer series in which they observed more lines of this series in mixtures of helium with relatively small amounts of hydrogen than could be detected in pure hydrogen.

Taking the mean of the experimental data recorded in Table II gives 16.0 volts as the ionization potential of hydrogen for the formation of  $H_2^+$ . As the  $H_2^+$  ion is probably unstable with respect to H and  $H^+$ , it must give off energy when it dissociates. If ionization could take place according to the scheme in Eq. (2) the ionization potential for such a process would then be less than 16.0 volts, assuming this to be the correct value, and the heat of dissociation would then be less than  $16.0 - 13.5 = 2.5$  volts, equivalent to 57,500 calories per mol. Langmuir,<sup>24</sup> Isnardi,<sup>25</sup> and Wohl,<sup>26</sup> by indirect methods obtained 84,000, 95,000 and 90,000 calories per mol respectively for this value. In view of the probable uncertainty of the values obtained by both these lines of investigation, we are not yet ready to assume that this discrepancy is a real one.

The several theoretical models for  $H_2^+$  give values for the ionization potential of  $H_2$  higher than the observed 16.0 volts. The Bohr model, considered untenable for other reasons, leads to the value 17.85 volts (2.20 Rh - 0.88 Rh), the Pauli<sup>27</sup> model to 23.7 volts, and the various models of Niessen<sup>28</sup> to values 23.5 to 28.8 volts.

DEPARTMENT OF CHEMISTRY,  
UNIVERSITY OF CALIFORNIA,  
February 9, 1925.

<sup>23</sup> Merton and Nicholson, *Proc. Roy. Soc.* **96A**, 112 (1919).

<sup>24</sup> Langmuir, *J. Am. Chem. Soc.* **34**, 860 (1912); Langmuir and Mackay, *ibid.* **36**, 1708 (1914); Langmuir, *ibid.* **37**, 417 (1915).

<sup>25</sup> Isnardi, *Zeits. Elektrochem.* **21**, 404 (1915).

<sup>26</sup> Wohl, *Zeits. Elektrochem.* **30**, 49 (1924).

<sup>27</sup> Pauli, *Ann. der Physik* **68**, 117 (1922).

<sup>28</sup> Niessen, *Physica* **2**, 345 (1922); *Ann. der Physik* **70**, 129 (1923).



## CRYSTAL STRUCTURE OF TITANIUM AND CHROMIUM\*

By R. A. PATTERSON

## ABSTRACT

Precision measurements of the crystal structure of these two metals in very pure form have been made. For chromium (99.8 percent) a body-centered cubic structure, with  $a_0 = 2.872\text{\AA}$ , is found; for titanium (99.9 percent) an hexagonal close-packed structure, with  $a_0 = 2.951\text{\AA}$ ; axial ratio  $c = 1.590$ . These structures are of the type previously assigned by A. W. Hull, but differ slightly in numerical values. They were measured in comparison with copper using Davey's value of  $a_0 = 3.597\text{\AA}$  for pure copper. The *densities* computed from these results come out 4.49 for Ti and 7.23 for Cr. Heat treatment had no effect on the crystal form for Ti, merely changing the size of the crystals.

## SPECIMENS

THE crystal structures of titanium and chromium have been determined using samples of pure metals. These samples were provided by M. A. Hunter who reduced the metals from pure chlorides with sodium.<sup>1</sup> The temperature of the reaction was sufficiently high to result in fusion—the metals coming out when cold in the form of pellets. These pellets were ground, washed, and then sprinkled in shellac on narrow ribbons of paper or cardboard. These ribbons constituted the specimens analyzed.

## METHOD

The standard x-ray diffraction apparatus developed by Hull and Davey was employed. It has been fully described in their papers.<sup>2,3</sup> The diffraction pattern due to chromium was accompanied on each spectrogram, for calibration purposes, by that due to copper. Each diffraction image is double, being produced by the  $\alpha_1$  and  $\alpha_2$  lines in the K spectrum of molybdenum, which have wave-lengths of 0.7078 and 0.7121 $\text{\AA}$ , respectively. It is possible by the application of a properly constructed scale to read off for each diffraction image the spacing of the set of planes giving rise to it, divided by the order of interference. This was done for each image produced by the  $\alpha_2$  radiation. The structure of copper is face-centered cubic and has been accurately measured by Davey.<sup>4</sup> Using his

\* The results of this paper were presented before the American Physical Society at the New York Meeting, February 28, 1925 (Phys. Rev. **25**, 581, 1925).

<sup>1</sup> M. A. Hunter, J. Am. Chem. Soc. **32**, 330 (1910).

<sup>2</sup> A. W. Hull, Phys. Rev. **10**, 661 (1917).

<sup>3</sup> W. P. Davey, J. Opt. Soc. Am. **5**, 479 (1921).

<sup>4</sup> W. P. Davey, Phys. Rev. **25**, 753 (June 1925).

value of  $a_0 = 3.597\text{\AA}$ , corrections due to any irregularities in the film were easily made. It was not necessary to locate the zero line on the film with the known diffraction pattern of copper present.

In the spectrograms of titanium, usually the two  $K\alpha$  lines of molybdenum were not resolved as they were in the case of chromium and copper. Consequently the centers of the diffraction images were read, and a negative correction of 0.25 percent was applied to each reading in order to obtain the value for the  $a_2$  radiation.

The use of copper instead of rock salt for a comparison pattern is recommended to those using this type of equipment for the following reasons. First, narrow flat wires can easily be made; second, these will give well defined diffraction images in which both  $\alpha$  lines are resolved throughout the length of the film; third, Davey has completed accurate measurements of the parameter for copper in terms of rock salt and has shown that the usual impurities in ordinary conductivity copper do not appreciably affect its lattice parameter.

#### DATA

Tables I and II contain the observed data for titanium and chromium respectively. In the first column are given the indices of the planes giving rise to each diffraction image. The numbers in the second column

TABLE I

*Results for titanium. Close-packed hexagonal structure.  
Sample used was 99.9 percent pure.*

Planes	Intensity	Plane spacing/order			
		Film 1	Film 2	Film 3	Film 4
10.0	4	2.556A	(2.540)A	2.551A	(2.544)A
00.1(2)	4	2.341	2.346	2.341	(2.335)
10.1	10	2.241	2.244	2.241	2.235
10.2	4	1.728	1.731	1.724	1.727
11.0	4	1.477	1.477	1.474	1.472
10.3	5	1.336	1.339	1.332	1.337
11.2	4	1.249	1.250	1.247	1.251
20.1	3	1.233	1.236	1.235	1.235
00.1(4)	1	1.176	1.176	1.173	(1.178)
10.1(2)	1	1.125	1.125	1.124	(1.121)
10.4	2	1.065	1.071	1.066	(1.069)
20.3	3	.989	.991	.989	.991
12.1	3	.942	.947	.945	.948
11.4	3	.917	.917	.918	.9185
10.5	1	.880	.884	.882	.881
10.2(2)	0	.849			
12.3	0	.8195	.820	.823	.822
30.2	0	.800			
Mean $a_0 =$		2.951A	2.954A	2.947A	2.951A
		Average $a_0 = 2.951\text{\AA}$			
Corresponding density = 4.49 gm/cc; density by Hunter and by Mixer = 4.50 gm/cc.					

specifying intensity are arbitrary, indicating relative order of intensities, but not ratios of intensities. To save space the average numbers for the films measured are given. The corrected plane spacings divided by the order of interference are recorded in the remaining columns. Each column represents a separate film and specimen. The application of a factor, computed from the geometry of the structure, to each plane spacing gives  $a_0$ , the side of the unit cell. At the foot of each column of plane

TABLE II  
Results for chromium. Body-centered cubic structure.  
Sample used was 99.8 percent pure.

Planes	Intensity	Plane spacing/order		
		Film 1	Film 2	Film 3
110	10	(2.052)A	(2.044)A	(2.037)A
100	4	1.436	1.435	1.436
211	8	1.172	1.174	1.173
110(2)	5	1.014	1.015	1.017
310	6	.909	.908	.909
111	2	.829	.830	.830
321	7	.768	.768	.769
100(2)	1	.718		.719
411, 110(3)	4	.6775	.6770	.6778
210	3	.6420	.6416	.6432
332	3	.6120	.6121	.6130
211(2)	3	.5865		.5870
431,510	4	.5630	.5645	.5632
Mean $a_0$ =		2.871A	2.873A	2.873A
		Average $a_0$ = 2.872A		
Corresponding density = 7.23 gm/cc;		density by Moissan = 6.92 gm/cc.		

spacings is given the average value of  $a_0$  as computed from that film. Only those values of the spacings that were obtained from clear cut diffraction images were used in the determination of the lattice parameters. The others are placed in parentheses.

## RESULTS

*Titanium.* The relative position of the diffraction images and their relative intensities indicate clearly the close-packed hexagonal structure for titanium, as previously found by Hull.<sup>5</sup> The axial ratio was determined by the graphical method of Hull and Davey,<sup>6</sup> to be  $1.590 \pm .002$ . The density from these measurements comes out 4.49, whereas Hunter and also Mixter obtained 4.50 gm per cc.

The diffuseness of the diffraction images and their lack of resolution are ascribed to the minuteness of the individual crystal grains—not to the powder grains.

<sup>5</sup> A. W. Hull, Science 52, 227 (1920); Phys. Rev. 18, 88 (1921).

<sup>6</sup> Hull and Davey, Phys. Rev. 17, 549 (1921).

Different specimens were subjected to different heat treatments in an endeavor to detect the existence of any other crystal structure between 0°C and 800°C. The four specimens that furnished the data in Table I were treated as follows:

Film 1: titanium had been dipped in liquid air.

Film 2: titanium had been heated to 850°C and quenched.

Film 3: titanium had been cooled 2½ hours in liquid air.

Film 4: titanium had been annealed at 850°C and cooled slowly.

No trace of polymorphism was found on any of these films. Some lines on Film 4 are resolved, indicating that long annealing at higher temperatures would permit further grain growth and higher resolution to be obtained.

*Chromium.* The diffraction patterns confirm the body-centered cubic structure for chromium previously found by Hull.<sup>7</sup> Sharp resolution and fair intensity extend across the film (through glancing angle of 45°) indicating that the crystal grains are sufficiently large to give higher orders of interference and good resolution, but not coarse enough to produce striated images. The computed density is 7.23 gm/cc, whereas Moissan gives 6.92 gm/cc.

The author wishes to express his thanks to Dr. M. A. Hunter for the pure metals and for many helpful suggestions, also his appreciation of the assistance rendered by Mr. W. C. Ellis and Mr. H. M. Faigenbaum in preparing specimens and in measuring films.

RENSSELAER POLYTECHNIC INSTITUTE,  
March 15, 1925.

<sup>7</sup> A. W. Hull, Phys. Rev. 17, 571 (1921).

PRECISION X-RAY MEASUREMENTS BY THE POWDER METHOD<sup>1</sup>

By F. C. BLAKE

## ABSTRACT

Corrections to x-ray spectograms obtained by the powder method.—Spectograms were obtained with a semi-cylindrical camera of radius 16.65 cm giving lines on both sides of the undeflected beam, using a powder sample about 0.2 mm in radius held in an accurately centered hole. *Correction for film shrinkage* was made by using Al as a comparison. *Correction for penetration into the sample.* This is taken to cause a shift of each line  $\delta l$  equal to  $d \cot \theta$ , and a value of  $d$  is chosen so as to make the lattice constant  $a_c$  computed from the various lines, approximately the same, or if the constant is assumed known, as in the case of Al, to make the computed radius come out constant. In one test with Fe, the greatest variation from the mean  $a_c$  was only .1 percent, taking  $d$  as .006 cm. With samples of varying radius  $r$ , the value of  $d$  was found to vary from +.006 cm ( $r = .15$  mm) to -.014 ( $r = .72$  mm). Hadding's method of correction is discussed. It is suggested that a combination of the two methods, taking  $\delta l = K_1 \theta \cot + K_2 r$ , would give even more accurate results.

Lattice constant for pure iron is found to be  $2.8603 \pm .0002A$ .

THIS paper is an attempt to carry the precision methods reported by Havighurst, Mack and Blake<sup>2</sup> one step further. These authors found it possible in large measure to avoid serious error in their crystal structure measurements by calibrating their films by means of some known standard, the standard being intimately mixed with the sample to be investigated.

This method of calibration proved to be thoroughly reliable but a comparison of the results obtained by these investigators with those of this paper shows the advantage to lie with the method here described. Phebus and Blake found the method of intimate mixing of standard and unknown substance unworkable in the case of alloys; therefore, another had to be found.

## DESCRIPTION OF APPARATUS

A water cooled x-ray tube with molybdenum target was surrounded with a cylindrical lead box somewhat after the manner of other experimenters.<sup>3</sup> A row of horizontal slits in the lead box allowed the free passage

<sup>1</sup> Presented before the American Physical Society as part of a paper by Phebus and Blake, Nov. 29, 1924 (Phys. Rev. 25, 107, 1925).

<sup>2</sup> Havighurst, Mack and Blake, J. Amer. Chem. Soc. 46, 2368 (1924).

<sup>3</sup> E. g. Davey, Gen. Elec. Rev. p. 565 (1922); also Bain, Chem. and Met. Eng. 25, 657 (1921).

of x-rays from the target. A second set of slits placed just in front of the sample under investigation prevented secondary rays from entering the cameras. The cameras differed from the cassette system of Davey only in two important respects. First, each camera had a septum down its middle to separate the lines for the standard from those for the unknown under investigation, the sample tube being filled with the powder of the standard at one end and with that of the unknown at the other. The sample tube itself was like those used by Havighurst, Mack and Blake.<sup>2</sup> Second, the cameras were semi-cylindrical in form, thus permitting a complete set of lines on both sides of the undeflected beam. The cameras had a radius of 16.65 cm. They were very carefully machined throughout, the usual sheet aluminum being on the outside of each camera and the photographic film being held tightly against this by elastic webbing. The hole for holding the sample under investigation was first bored and then the walls of the camera were turned true in the lathe. This insured that each sample was accurately at the center of the photographic film.

The double displacements between corresponding lines were determined by means of a specially built comparator reading to 0.02 mm. Thus, except for errors of judgment in estimating the centers of lines, the displacement of a line from the zero was measured for aluminum to within 1 part in 5,000 for the nearest line and 1 part in 18,000 for the line farthest removed from the main central beam.

#### SOURCES OF ERROR

The two chief sources of error which must be eliminated or corrected for in precision work are (1) the unequal shrinking of the photographic films, along with the influence of humidity upon their length and (2) the influence of the substance of the sample upon the absorption of the x-rays and consequently upon the registering of the rays upon the film. The first source of error is corrected for by calibrating the film by means of the standard whose space lattice is known, provided the inequality of absorption of the rays in the standard and in the unknown can be corrected for. If the proper correction for penetration can be found it must make the lattice dimensions independent of the glancing angle and independent of the diameter of the specimen under investigation. As will be seen this has been done.

#### CORRECTION FOR PENETRATION INTO THE SAMPLE

In the precision work of Blake and Duane<sup>4</sup> in determining the value of the quantum of action by means of x-rays it was found that the penetra-

<sup>4</sup> Blake and Duane, *Phys. Rev.* 10, 624 (1917).

<sup>6</sup> Blake, *Proc. Nat. Acad. Sci.* 4, 237 (1918).

tion of the rays into the crystal introduced a serious error into the measurements unless it was obviated. This was done by having over the axis of the spectrometer not the front face of the crystal but the "effective plane" of the crystal. The effective plane was defined by them as that plane in the crystal at which if all the rays were diffracted into the ionization chamber, the ionization current would be the same as that due to the sum of all the diffractions at the various planes of the crystal. The writer<sup>5</sup> at the time derived theoretically an expression for the depth of the effective plane below the surface of the crystal that agreed entirely with the value found experimentally by Blake and Duane in the case of calcite. The correction formula for penetration into the sample used in this paper is based on similar ideas.

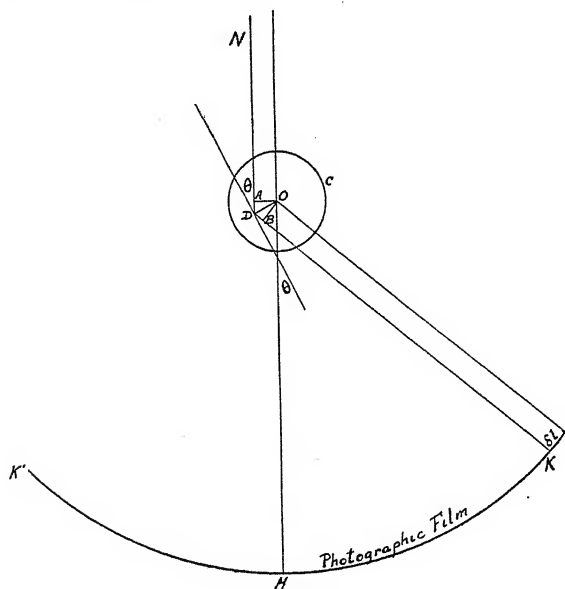


Fig. 1

In Fig. 1,  $O$  is the center of the sample under investigation,  $OC$  being the radius;  $O$  is also the center of the photographic film. Let  $AD$  be the distance of the effective plane below or above the center  $O$ . The central ray of the x-ray beam passes along  $OH$ . If  $H$  is the center of the undeflected beam and  $K$  is the position of the center of some line on the film, then  $HK = \frac{1}{2}KK'$  where  $K'$  is the position of the mate of the line on the other side of the undeflected beam, assumed to be the same distance from  $H$ . Now the effective plane is defined as the plane from which the center of the line at  $K$  is reflected.

Then if  $OA$  and  $OB$  are normal to the incident and reflected rays respectively, we have  $OA = OB = d \cot \theta$  where  $\theta$  is the glancing angle and  $d = AD$ . Obviously, all lines on the film in order to give the same space lattice must be referred to the center  $O$ . Putting  $HK = l$ , if the so-called radius  $OH$  of the camera is large compared to  $d$ ,  $OB = \delta l$  very approximately, where  $\delta l$  is the correction to be applied to half the measured distance on the film between corresponding lines.

By inserting a zirconium oxide filter into each camera the x-rays are rendered monochromatic, only the  $K\alpha$  doublet of molybdenum appearing on the film. In view of this fact, it seems probable that  $d$  should be the same for all the lines on the film; for so far as registering is concerned the average depth of penetration into the sample is certainly independent of the orientation of the minute crystals in the sample. If this is so then  $\delta l$  is proportional to  $\cot \theta$ . It would appear at once that the correction factor  $d \cot \theta$  would become absurdly large for very small values of  $\theta$ , but it will be shown at the end of this paper that the true correction factor for substances easily penetrated by x-rays is  $K \cot \theta \delta \theta$  where  $\delta \theta$  is the angular width of each line; and while  $\delta \theta$  is roughly constant for the different lines it does decrease with  $\theta$  and thus prevents the correction becoming inordinately large for small angles. Experiments are now under way to test this with crystals having large space lattices in one direction at least. For those crystals studied to date, however, the error introduced in taking  $d$  constant instead of taking it proportional to the angular width of the lines is just barely outside the limit of experimental error of measurement.

#### TEST OF THE CORRECTION FACTOR FOR PENETRATION

A test of the correctness of the formula for  $\delta l$  can be seen illustrated in Table I. Aluminum was used as a standard to determine the space lattice of iron, aluminum itself having been previously found to have a space lattice constant of  $4.0438 \pm 0.0002\text{\AA}$ , by checking against very pure sodium chloride. The aluminum was "Baker analyzed," containing 0.02 percent  $\text{SiO}_2$  and 0.01 percent Fe. In the light of the evidence submitted by Havighurst, Mack and Blake<sup>2</sup> on the effect of impurity upon space lattice it is clear that both the salt and the aluminum were effectively pure. The density of the aluminum used was 2.7068, this determination being made with a set of weights certified by the Bureau of Standards, conductivity water being used and buoyancy correction applied. Error due to surface tension of the suspending wire was eliminated. The calculated density was found to be 2.7104 using Richards'



value for the atomic weight of aluminum and Millikan's value for the mass of the hydrogen atom, viz., 26.96 and  $1.662 \times 10^{-24}$  gm. From the measured density the space lattice is computed to be 4.0456, which differs from the measured value by 0.045 percent, the accuracy being of course greater than that to which the mass of the hydrogen atom is known.

Table I gives for aluminum the measured displacement  $l$ , which as in all the tables is half of the double displacement, and  $l_c$  the corrected value of  $l$  where  $l_c = l + d_1 \cot \theta$ . By trial  $d_1$  was chosen so as to make the camera radius  $r_c$  constant,  $r_c$  being equal to  $l_c/2\theta$  where  $\theta$  satisfies Bragg's well-known equation. The uncorrected radius  $r$  computed from the values of  $l$  is also given. The greatest percent of variation from the mean value of  $r_c$  is 0.09.

TABLE I  
Results for aluminum and iron  
Diameter of samples 0.378 mm;  $d$  taken as .005 cm for Al and .006 cm for Fe.

Aluminum					Iron				
Face	$l$ (cm)	$l_c$ (cm)	$r$ (cm)	$r_c$ (cm)	Face	$l$ (cm)	$l_c$ (cm)	$a$ (cm)	$a_c$ (cm)
111	5.072	5.105	16.612	16.722	110	5.869	5.903	2.8763	2.8598
200	5.873	5.901	16.638	16.718	200	8.374	8.397	2.8661	2.8584
220	8.377	8.397	16.691	16.732	211	10.325	10.344	2.8626	2.8574
311	9.876	9.892	16.713	16.741	220	12.008	12.024	2.8582	2.8546
222	10.326	10.342	16.708	16.735	310	13.498	13.512	2.8591	2.8564
400	11.990	12.003	16.708	16.726	222	16.164	16.176	2.8590	2.8570
331	13.123	13.135	16.709	16.725	411	18.554	18.564	2.8600	2.8587
420	13.487	13.498	16.714	16.728	330				
422	14.867	14.871	16.714	16.725					
333	15.838	15.848	16.715	16.728					
440	17.374	17.383	16.716	16.725					
531	18.255	18.263	16.714	16.721					
442	18.542	18.550	16.712	16.718					
			Mean	16.726				Mean	2.8575

Using the mean corrected camera radius one can determine the space lattice for iron,  $a$  uncorrected and  $a_c$  corrected. Here the iron lines were corrected by an amount  $\delta l = d_2 \cot \theta$  where  $d_2$  was found by trial to be 0.006 cm. Just as column 5 is a great improvement over column 4 so is column 10 a great improvement over column 9, the greatest percent of variation from the mean value of  $a_c$  being 0.10.

Of course it does not yet appear that there may not be some systematic error in all of the results of Table I, a table which is typical of the degree of reproducibility of the results both of this paper and of the paper of Phebus and Blake.

#### PENETRATION CORRECTION FACTOR AS A FUNCTION OF SAMPLE DIAMETER

To reduce the chance of a systematic error in the measurements it was thought worth while to investigate the influence of sample diameter upon

the penetration and to determine its correction factor. The diameter of the sample was varied from 0.25 mm to 1.45 mm by steps, using aluminum as a standard and iron as unknown, great care being taken in each case to have the sample properly centered in the camera. Table II gives the results for iron uncorrected for penetration, the camera radius as de-

TABLE II  
*Results for iron uncorrected for penetration.*

Diam. of sample	$r_c$	Edge of iron cube in angstroms for various faces							Mean
		110	200	211	220	310	222	321	
0.276mm	16.592cm	2.8694	2.8658	2.8606	2.8589	2.8572	2.8572	2.8570	2.8609
0.378	16.726	2.8763	2.8661	2.8626	2.8582	2.8591	2.8590	.....	2.8635
0.586	16.724	2.8564	2.8569	2.8565	2.8588	2.8591	2.8584	2.8571	2.8576
0.798	16.604	2.8404	2.8538	2.8532	2.8528	2.8540	2.8527	2.8525	2.8514
1.045	16.585	2.8382	2.8456	2.8469	2.8483	2.8524	2.8487	2.8530	2.8476
1.442	16.726	2.8166	2.8316	2.8352	2.8392	2.8381	2.8406	2.8466	2.8354

termined by aluminum being corrected, however, in the manner indicated above. This table shows very plainly the need for a proper correction for penetration.

When this correction is applied the results obtained are as indicated in Table III. It will be noticed that the true space lattice for iron is here shown to be entirely independent of sample diameter for samples less than 1 mm in diameter.

TABLE III  
*Results for iron corrected for penetration.*

Sample diam. (mm)	$d_1$ (Al) (cm)	$d_2$ (Fe) (cm)	$r_c$ (cm)	Edge of iron cube in angstroms							Mean
				Deviation from each mean in angstroms $\times 10^4$							
				110	200	211	220	310	222	321	
0.259	.003	.006	16.658	+ 7	+ 5	- 5	- 6	-10	.....	- 1	2.8570
0.276	.003	.004	16.592	- 2	+17	-19	-25	-11	+12	+ 2	2.8575
0.378	.005	.006	16.726	+26	+13	+ 2	-26	- 8	.....	- 2	2.8572
0.502	.006	.004	16.713	- 4	- 1	- 2	+16	+12	+ 2	-25	2.8571
0.586	.006	.000	16.724	-12	- 6	-11	+12	+15	+ 8	- 5	2.8576
0.593	.004	-.001	16.605	+22	+10	- 7	-31	-16	-10	0	2.8579
0.678	.003	-.004	16.595	0	+12	-28	- 9	- 3	+20	+ 3	2.8576
0.798	.003	-.0055	16.604	+ 6	+45	+ 8	-30	- 3	-21	-14	2.8575
0.798	.003	-.004	16.592	+ 1	+23	+ 2	-22	+ 8	-19	+ 5	2.8582
1.045	.004	-.007	16.585	(+28)	(+ 6)	(-13)	(-17)	(+14)	(-28)	(+ 8)	(2.8543)
1.442	.004	-.014	16.726	(+47)	(-32)	(-13)	(-16)	(+27)	.....	(-13)	(2.8501)
Final mean 2.8575 $\pm$ .0002A											

Plotting the depth of the effective plane  $d$  against the diameter of the sample gives the curves of Fig. 2, the values for Al being indicated by crosses, those for Fe by circles. The curve for aluminum is seen to be a horizontal straight line, that for iron to be a straight line having a large

slope. No attempt was made to determine  $d$  closer than to within 0.0005 cm, for the final individual results of Table III have the actual errors of measurements on the double displacement still in them.

Since one has no good check on the density of the powder in the sample tube it is not surprising that both for aluminum and for iron the penetration correction factor has points apparently badly off the curve. Obviously, an accurately linear relation could only be expected if all samples had the same density of packing in the sample tube.

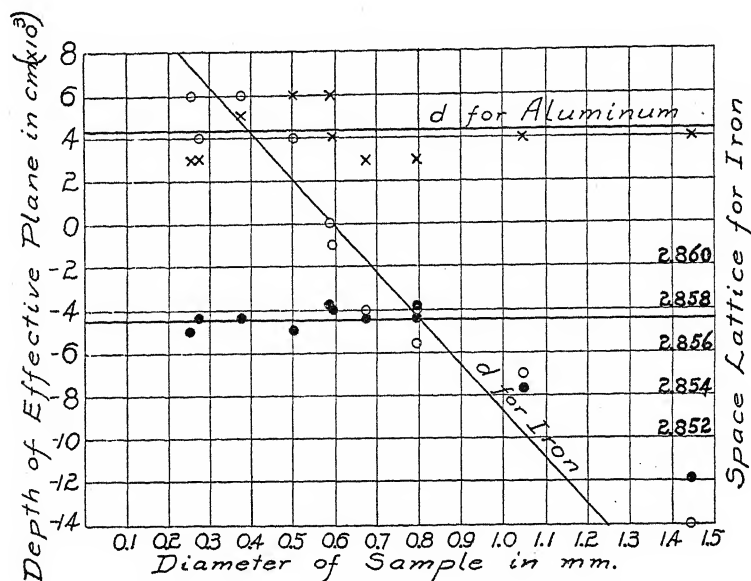


Fig. 2. Variation of  $d$  with diameter of sample.

The results of the last column of Table III are also plotted as a function of diameter in Fig. 2 using black dots, and here it is worth while noting that the points are closer to a straight line up to 0.8 mm than are the points for the other two curves. As shown by Table III the edge of the iron cube is 2.8575 within one part in 15,000, taking the mean wavelength of the  $K\alpha$  doublet of molybdenum as 0.71000Å, which is the mean value given by Duane<sup>6</sup> as accurate to 1 part in 35,000.

Chemical analysis of the iron used in investigating the effect of sample diameter upon spacing measurements showed the iron to have carbon as an impurity. Hence this iron was checked in two ways against Burgess pure electrolytic iron which is purer than Baker's analyzed iron wire used for standardization purposes and contained no carbon whatever.

<sup>6</sup> Duane, Nat. Res. Coun. Bull. 1, Pt. 6, p. 394.

First, both specimens of iron were inserted in the same sample tube and an exposure made. Second, the pure iron was run against pure sodium chloride as a standard. The results were 2.8605 and 2.8601 (mean 2.8603) on the Duane standard of wave-length.

An inspection of Table II shows that unless one desires to press the degree of accuracy to that given in this paper he will make but a small error in his result by ignoring entirely the diffraction lines nearest the center of the film and taking the mean of the last three or four lines only, provided the ratio of the radius of the camera to that of the sample is at least 500; for it will be noted that the mean of the readings for the faces 220, 310, 222 and 321 for the first three rows of Table II is 2.8581 which is not far from the true value for 0.7100A, viz., 2.8576. A second proviso here is, of course, that the camera radius is corrected for in the manner indicated.

#### CRITICAL DISCUSSION OF CORRECTION FACTORS IN POWDER METHOD

Hadding<sup>7</sup> has discussed the disturbances in the line distances and in the breadth of lines in the powder method and has derived the formula

$$2l_c = 2l - r_0(1 + \cos 2\theta)$$

in which  $l$  and  $l_c$  have the meanings given in this paper,  $r_0$  is the sample radius and  $\theta$  the glancing angle. He states that this formula holds when the secondary (the diffracted) rays are excited only on the surface of the sample, i.e., for strongly absorbing substances. It should be noted that the correction for line distance is negative and varies from  $2r_0$  to 0 as  $\theta$  increases from 0 to  $\pi/2$ . Using Bragg's value for the space lattice of iron pyrites and the well known value for the lattice constant of rock salt, Hadding calculates the distance between corresponding lines and compares them with the measured distances on a film of camera radius 5.05 cm, getting differences varying from -1.9 mm to -1.1 mm for pyrites and -1.4 mm to 0.0 mm for rock salt, the diameter of the sample in both cases being 2 mm and a copper anticathode being used. He then remarks that for those cases where the rays penetrate further into the sample the difference between calculated and measured values lessens. It does not appear from his discussion that the correction factor can change sign as the writer has found it to do for iron as the sample radius changes. Hadding states that if the measurements for the double displacement are taken from the outer edges of the lines instead of from their centers that no correction is needed for absorption or penetration, but that there will always be a constant difference between calculated and measured line

<sup>7</sup> Hadding, *Centralblatt f. Min. etc.* p. 631 (1921).

distances equal to the diameter of the sample. Hadding therefore states the following rule: Measure all line distances from the outer edges of the lines and subtract the sample diameter from each of these distances. No support of the rule is given from experimental measurements.

It was deemed worth while to test Hadding's rule in the case of one of the films for aluminum and iron, so one out of several films taken for sample diameter 0.798 mm was chosen. The centers of the lines were carefully measured as were also their outside edges, these measurements

TABLE IV  
*Comparison of methods of correction for penetration*

Blake's method						
Face	Aluminum ( $d_1 = .002$ )			Face	Iron ( $d_2 = -.004$ )	
	$l$	$l_c$	$r_c$		$l$	$a_c$
111	5.051	5.064	16.588	110	5.887	5.865
200	5.839	5.850	16.574	200	8.337	8.321
220	8.302	8.310	16.559	211	10.278	10.265
311	9.793	9.800	16.586	220	11.923	11.912
222	10.244	10.250	16.586	310	13.408	13.399
400	11.882	11.887	16.565	222	16.066	16.059
331	13.012	13.017	16.575			Mean: 2.8544
420	13.371	13.376	16.577			
422	14.727	14.731	16.567			
333	15.700	15.704	16.577			
		Mean: 16.575				

Hadding's method (radius of sample = .040)						
Face	Aluminum			Face	Iron	
	$l$	$l_c$	$r_c$		$l$	$a_c$
111	5.115	5.075	16.624	110	5.923	5.883
200	5.912	5.872	16.636	200	8.385	8.345
220	8.385	8.345	16.629	211	10.325	10.285
311	9.883	9.843	16.658	200	11.981	11.941
222	10.306	10.266	16.612	310	13.501	13.461
400	11.950	11.910	16.597	222	16.144	16.104
331	13.100	13.060	16.630			Mean: 2.8544
420	13.451	13.411	16.620			
422	14.810	14.770	16.611			
333	15.788	15.748	16.623			
		Mean: 16.624				

being taken  $2\frac{1}{2}$  months later than the first measurements on the film. The results are shown in Table IV. In this table many of the headings are the same as in Table I. Following Hadding's rule for measurements by his method  $l_c = l - r$  where  $r$  is the sample radius. The agreement for the space lattice is seen to be exact although the individual readings differ somewhat. It should be noted that the so-called radius of the camera was by the method of this paper 16.575 cm, by Hadding's method 16.624 cm,

and that the maximum variation from the mean for this radius was somewhat greater in Hadding's method. A further check on Hadding's method was made on the sample of diameter 0.378 mm and the two methods agreed to within 0.07 percent. However, the maximum variation in the radius of the camera by Hadding's method was 0.38 percent while by the method here reported on it was only 0.11 percent. On the iron lattice the maximum variations by the two methods were respectively 0.35 and 0.19 percent. It seems to the writer that Hadding's method is bound to give considerable variations in quantities that one ought to expect to be constant for the reason that the width of a line is dependent upon its intensity. It ought to be stated that when the indicator line of the comparator was put on the outside of even the most intense line of any film it was easy to note with the unaided eye that the point of maximum intensity was considerably removed from this edge.

The writer regards this agreement between the two methods as a strong support of the ideas concerning penetration contained in this paper. He wishes to emphasize the fact that the correction factor may be either positive or negative, depending upon the thickness of the sample. Over a wide range it is always positive for elements of low atomic number like aluminum and sodium, always negative for heavy elements like lead. As shown for iron, it changes sign for intermediate elements.

#### A SECOND CORRECTION FACTOR\*

If one plots against the glancing angle the space lattice of iron as given for each line in Table III, the fact is revealed that the correction factor  $d \cot \theta$  tends to make the value of the lattice constant slightly too large for the first two lines and slightly too small for the next three. The difference is slight but beyond the limits of error so an attempt has been made to find a correction factor in an entirely different way.

It is well known that the absorption of x-rays is proportional to the third power of the wave-length. Suppose both edges of any line on the film are measured. Call  $A$  the absorption. Then it follows from the law of absorption that  $\delta A/A = 3 \cot \theta \delta \theta$ , since the wave-length varies as  $\sin \theta$ . This means that for substances that are easily penetrated ( $d$  positive) the inner edge of each line is displaced by an amount which is proportional to  $\delta A/A$  toward the direction of smaller values of  $\theta$ . Thus, the true correction factor should be proportional to  $\cot \theta \delta \theta$ .

Suppose on the other hand that the rays are only very slightly penetrating. Then, following Hadding, an amount  $\delta l = r$ , the radius of the

\* This section was added May 18, 1925—Ed.

sample, should be subtracted from all readings on the film. In the case of a sample that is partially penetrated by the rays, obviously, the proper correction consists of two parts, one depending upon penetration and the other depending upon absorption; and there is evidently a mean condition of no correction where these two corrections balance each other (equivalent to saying  $d=0$ ).

An attempt has been made to apply the alternative correction to the aluminum lines for the second sample of diameter 0.798 mm of Table III. This method wholly eliminates the slight lowering of the space lattice obtained from the middle lines spoken of above and so may be regarded as an improvement.

The bearing of the ideas presented in this paper upon the question of the so-called index of refraction of substances to x-rays will be discussed in another paper.

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MENDENHALL LABORATORY OF PHYSICS,  
OHIO STATE UNIVERSITY,  
March 19, 1925.



## THE SCHOTTKY EFFECT IN LOW FREQUENCY CIRCUITS

BY J. B. JOHNSON

## ABSTRACT

(1) *In the absence of space charge.* This effect, discovered by Schottky, which depends on the probability fluctuations of electron emission from a filament, has been measured over a considerable range of conditions in resonant circuits of which the natural frequency was varied from 8 to nearly 6000 p.p.s. The effect is much larger in the lower range of frequencies than the theory predicts. *With a tungsten filament,* the ratio of observed to theoretical effect  $e'/e$  is about .7 for frequencies above 200, but increases rapidly to 50 at 10 cycles per sec. *With an oxide coated filament,* the ratio increases from 1 at 5000 cycles to 100 at 100 cycles. This is interpreted to mean that the emission of electrons is not strictly chaotic but is influenced by irregular temporal changes in the cathode emissivity. In a high frequency circuit these changes become imperceptible and the emission is effectively random. (2) *When current is limited by space charge* the Schottky effect decreases because of the interaction of the electrons, and other disturbances may act upon the space charge so as to completely mask the remanent Schottky effect. The magnitude of the disturbances in amplifying vacuum tubes can therefore not be predicted from measurements on the true Schottky effect.

THE thermionic current in a vacuum tube is not a smooth flow of electricity, but is subject to rapid and irregular fluctuations in magnitude. These fluctuations, discovered by W. Schottky and called by him the "Schrot-Effekt" (small shot-effect) are caused by the *random* emission of electrons from the cathode, and are made manifest by voltage or current fluctuations in any circuit into which the tube is connected. When these irregularities are sufficiently amplified by other vacuum tubes to be perceivable by means of a telephone receiver, they give rise to a continual sound with no definite pitch, like that usually associated with the conch shell, or like the faint sound that is heard when the hand is cupped to the ear.

The mathematical theory of the Schottky effect<sup>1</sup> is based upon the assumption that *the electrons pass from the cathode to the anode of the tube independently of one another.* Interpreting this condition by the simple laws of probability, it has been shown that the magnitude of the fluctuations of voltage or current in the circuit associated with the tube should depend only upon the charge on the electron, the average space current,

<sup>1</sup> W. Schottky, Ann. der Phys. 57, 541 (1918); idem. 68, 157 (1922).

J. B. Johnson, Ann. der Phys. 67, 154 (1922).

T. C. Fry, J. Franklin Inst. 199, 203 (Feb. 1925).



and the circuit constants. This prediction has hitherto either failed of verification<sup>2</sup> or has been verified only in part.<sup>3</sup>

It is the purpose of this paper to present the results, first, of a considerable series of measurements on the Schottky effect as it appears in circuits of comparatively low natural frequency, and secondly, of some preliminary studies upon the possible relation between the Schottky effect and the "noise" in vacuum tube amplifiers.

The measurements made under the conditions in which the Schottky effect should appear, i.e., in two electrode tubes with no appreciable space charge, show some striking deviations from the theory. While in the higher range of frequencies that were studied or with very low space currents the effect approached the predicted value, at the lower frequencies it is much too large. Particularly interesting is the behavior of oxide coated cathodes which give an effect up to hundreds of times too large at the lowest frequency, remarkable when we consider that this state of affairs can only be caused by a sequence of electron emissions different from the postulated purely random one. Except for the fact that this larger effect varies with the frequency and the space current, the circuit responds to it much the same as to the purer Schottky effect at the higher frequencies.

In amplifier tubes on the other hand, space charge is always present and makes the electrons pass in a sequence more orderly than the purely chaotic one. In fact, in these tubes the Schottky effect is so profoundly affected by the presence of space charge that even in the same tube there is little correlation between the noise with and without space charge. Furthermore, when space charge limits the current in a tube the opportunity also exists for agencies to come into play that can alter the current by acting upon the space charge. Tungsten filament tubes are usually subject to disturbances of this kind, so large and frequent that they entirely mask the reduced Schottky effect. Wehnelt cathodes are much less productive of this kind of disturbance so that consistent measurements can be obtained with tubes having oxide coating filaments.

The measurements here reported were done with apparatus in which the final indicating instrument was a thermocouple and micro-ammeter. Since the measured effect did not in general agree with the theory, the

<sup>2</sup> C. A. Hartmann, *Ann. der Phys.* **65**, 51 (1921); *Phys. Zeits.* **23**, 436 (1922). Hartmann's method of measurement could not give correct results, as pointed out by R. Fürth (*Phys. Zeits.* **23**, 354, 1922).

<sup>3</sup> A. W. Hull and N. H. Williams, *Science*, Aug. 1, 1924, p. 100; *Phys. Rev.* **25**, 147 (Feb. 1925). These authors obtained a check with the theory using a circuit of high natural frequency.

measurements were carried out for a number of tubes and covered a considerable range of frequencies, current values and circuit constants. The evaluation of the data was done according to the exact relation derived by Fry rather than by the approximate formula of Schottky.

#### METHOD OF MEASUREMENT AND COMPUTATION

For the purpose of measuring the Schottky effect the space current of the tube was passed through the inductance and resistance of a damped resonant circuit. The voltage fluctuations set up across this circuit were amplified with comparatively small distortion, by an amplifier<sup>4</sup> which terminated in a vacuum thermocouple and micro-ammeter. The measuring system therefore indicated the effective square of the voltage surges over the resonant circuit.

This measuring circuit, comprising the amplifier and thermocouple, was calibrated by sinusoidal alternating voltage over the whole range of frequencies of the variable resonant circuit, extending from about 8 p.p.s. to nearly 6000 p.p.s. The calibrating voltage was obtained from a vacuum

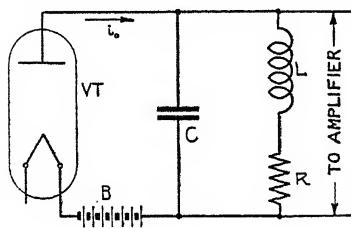


Fig. 1. Experimental circuit.

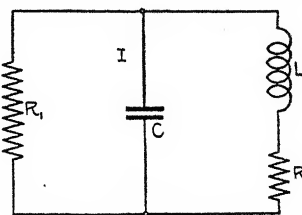


Fig. 2. Equivalent experimental circuit.

tube oscillator and was attenuated to the necessary small fraction of a measured initial value by a two-step resistance potentiometer. The resistances in this network were arranged and shielded with special care with a view to avoiding induction effects between the branches.

The circuit immediately connected to the experimental tube is shown diagrammatically in Fig. 1. The tube itself is represented by  $VT$ ,  $B$  is a dry cell battery, usually of 360 volts, while  $L$ ,  $C$  and  $R$  are the inductance coil, condenser and resistance in the resonant circuit. The condenser  $C$  was a mica condenser of negligible effective resistance. It was variable in steps from  $1\mu f$  to  $.001\mu f$ . For the lowest frequencies this was supplemented by paper condensers of up to  $7.5\mu f$  capacity of known effective resistance. The resistance  $R$  was a non-inductive decade box. For the

<sup>4</sup> The amplifier consisted of four stages with Western Electric 102-D tubes and one stage using a 101-D tube, all resistance-capacity coupled. The total voltage amplification was about  $3 \times 10^5$  and the power amplification was  $10^{14}$ .

inductance  $L$  four separate coils were used, each calibrated over the pertinent range of frequency and direct current value for effective inductance and series resistance. One of these coils,  $A$ , whose inductance was .100 h, was wound on a toroidal wood core. The other three were wound on cores of silicon steel with air gaps, and their inductances were about .1 h, .025 h, and 38 h, respectively and will be referred to as coils  $B, C$  and  $D$ .

The experimental circuit includes also the input elements of the amplifier, but electrically it can be represented by Fig. 2. In this diagram  $R_1$  is the resultant of three resistances in parallel, namely, the resistance to alternating current of the experimental tube at any particular condition, the grid leak resistance of the first amplifier stage and the effective input shunt resistance of the tube in this stage. In the value of  $C$  must be included also the input capacity of the first amplifier stage, usually negligible. These various values were obtained by suitable measurements.

The measurements that were made upon the Schottky effect in this circuit will, in what follows, be expressed in terms of the mean square voltage  $\bar{V}^2(\text{obs.})$  across the resonant circuit at the input of the amplifier. This quantity is given simply by the product of the deflection of the thermocouple meter (less the zero reading caused by inherent amplifier noise) and the calibration constant of the measuring system, which was calibrated in terms of voltage squared.

This measured quantity is to be compared with the corresponding quantity  $\bar{V}^2(\text{calc.})$  which is obtained from the known conditions and circuit constants as shown by Fry.<sup>1</sup> Fry has developed a general formula for the Schottky effect which is applicable to any circuit. However, the specific example given by Fry covers exactly the arrangement of apparatus shown in Fig. 2, so that his Formula (13) can be used directly in this case. With certain changes in the notation,<sup>5</sup> made for convenience in the presentation, this formula reads,

$$\bar{V}^2(\text{calc.}) = \frac{ei_0}{2C^2} \frac{L}{R(1+L/RR_1C)} \left[ 1 + \frac{C}{L} \frac{R^2}{(1+R/R_1)} \right].$$

in which

$e$  = charge on the electron;

$i_0$  = average space current;

$L$  = effective inductance;

$C$  = total capacity;

$R$  = effective resistance in the inductance branch;

<sup>5</sup> Fry's formula is expressed in terms of  $S$ , the mean power in the thermocouple, instead of the mean square voltage over the resonant circuit.

$R_1$  = total shunt resistance, including that of the experimental tube, grid leak and amplifier tube.

Great accuracy was not striven for in this work because of the large differences found to exist between measurements and theory. Taking into account all the possible sources of error which could enter the observations, calibrations and measurements of circuit constants, the probable error of a single comparison between an observed and a calculated value of  $V^2$  is about five percent.

#### PROCEDURE AND RESULTS

For certain preliminary work the thermocouple in the measuring circuit was replaced by a pair of telephone receivers which could also be connected to a variable source of current giving a sound similar in character to that produced by the amplifier. By the use of this modified circuit a considerable number of tubes were examined under identical conditions in order to determine qualitatively the influence of structural factors upon the amplitude of "noise" produced when the space current is limited by the cathode temperature so that space charge is practically absent. These tubes differed from one another, in the first place, as to the arrangement of the electrodes, some being standard audions while others were special tubes having the cathode and anode in various dispositions. Some of the tubes had the electrodes insulated with extreme care, and one tube had the electrodes enclosed in a grounded metal cylinder so that no part of the glass was exposed to the light or the electron current from the filament. The anode material was nickel in most of the tubes, but in some platinum or tungsten was used. The tubes had filaments of different materials such as platinum coated with rare earth oxides by various methods, commercial tungsten, pure tungsten and single crystal tungsten.

In the amplitude of sound which they produced these tubes differed from one another considerably, by factors perhaps as large as ten. Among all the variables, however, only that of the filament material showed a definite correlation to the sound. The sound from the tubes with oxide coated filaments was on the average several times larger than that from the tungsten filament tubes, but of the same quality so far as could be judged. In one tube the gas pressure was varied while the sound was observed, but there was no appreciable increase in the loudness until the pressure was so high that a glow began to be visible in the tube. In another case the tube was exposed to various amounts of illumination without any effect on the sound.

From the tubes thus tested, three were selected as representative of their groups, for the quantitative measurements. Two of these tubes were standard Western Electric 102-D audions with plane-parallel plates and grids and a V shaped ribbon of oxide coated platinum as cathode. These will be referred to as tubes No. 2 and No. 3. Tube No. 1 was similar in structure but had a filament of pure tungsten. When they were used as two-electrode tubes the grid and plate were connected together so as to form but one anode.

The results of the observations on these tubes will be presented so as to show the relation between the observed and the calculated value of  $\bar{V}^2$ , first as the circuit constants  $C$ ,  $L$  and  $R$ , the natural frequency of the resonant circuit, and the space current  $i_0$ , are varied in the absence of space charge; and secondly, as space charge limits the current in the two-

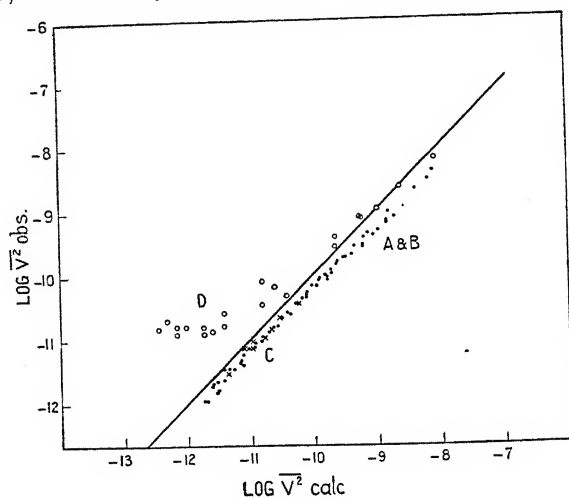


Fig. 3. Capacity and inductance variation for tube No. 1, tungsten filament; current 5 m-a.; various inductances A, B, C and D; frequency 8 to 6000 p.p.s.

electrode or three-electrode tube. The solid line in the diagrams is in each case the locus of the theoretical value of  $\bar{V}^2$ . The letters A, B, C and D on the diagrams refer to the inductance coils that were used in the resonant circuit for the groups of points which the letters designate.

#### A. THE SCHOTTKY EFFECT IN THE ABSENCE OF SPACE CHARGE

In Figs. 3 and 4 is shown the relation of the observed to the calculated values of  $\bar{V}^2$  for tubes No. 1 and No. 2 respectively, the capacity of the resonant circuit being varied between the limits  $7.5\mu\text{f}$  and  $.01\mu\text{f}$ . The observations for the tungsten filament tube with the smaller inductance lie nearly parallel to the theoretical line but somewhat below it, as if the

charge of the electron were about two-thirds of what it is known to be. With the 38 henry coil the observed values of  $\bar{V}^2$  become increasingly too high with increasing capacity, being about 50 times larger than the

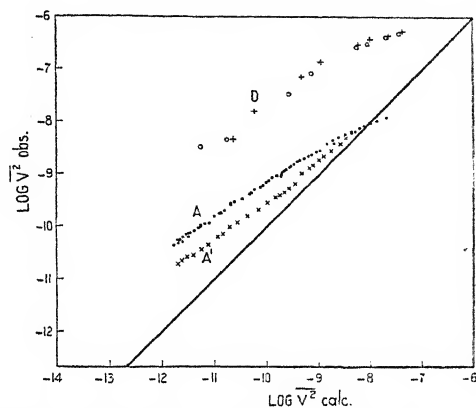


Fig. 4. Capacity and inductance variation for tube No. 2, coated filament; current 5 m-a.; two inductances A and D. Curve A' was taken at a different time.

theoretical value at the largest capacity. The oxide coated filament tube yielded values that are too high over nearly the entire range and approach the theoretical values only at the lower capacities. Oxide filaments also

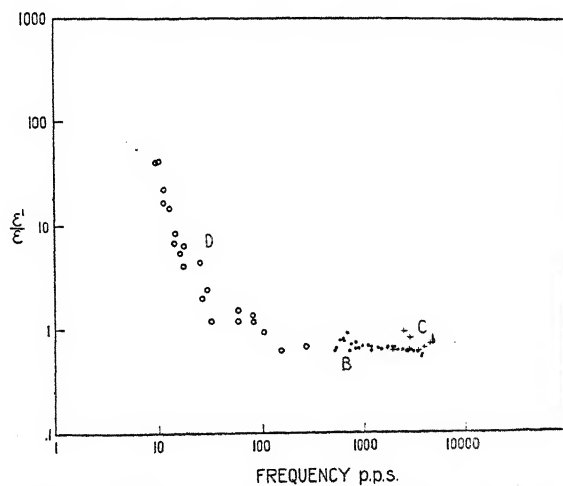


Fig. 5. Frequency variation for tube No. 1, tungsten filament; same data as in Fig. 3 plotted to frequency scale.

show a greater change with time than has been observed with tungsten filaments, as illustrated by the curves A and A' of Fig. 4, obtained with the same tube under identical conditions but at different times.

The variable which causes the divergence from linearity of the curves of Fig. 3 and Fig. 4 and which does not appear in the theory is the frequency of the resonant circuit. This is definitely shown upon plotting to a frequency scale, as has been done for the previous data in Figs. 5 and 6, and in Fig. 7 for other data. The ordinates are the ratios of the apparent to the actual charge of the electron, which is the same as the ratio of the observed to the calculated values of  $\bar{V}^2$ . The logarithmic scales of Figs. 5 and 6 cover a larger range, while the linear scale of Fig. 7 brings

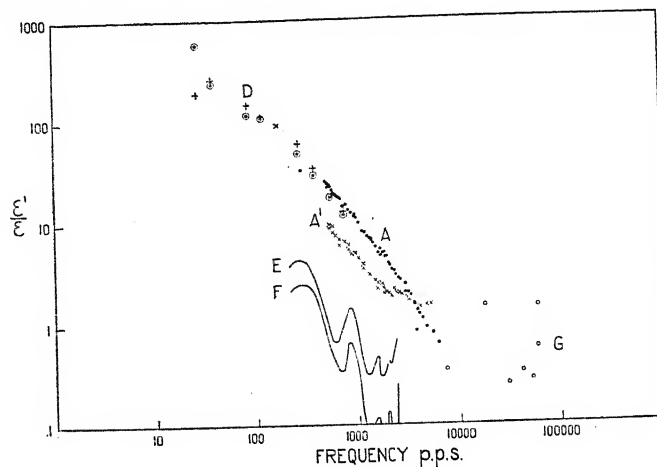


Fig. 6. Frequency variation for tube No. 2, coated filament; same data as in Fig. 4 plotted to a frequency scale; curves E and F give Hartmann's results for 2 m-a. and 20 m-a.; points G were obtained with less steady measuring circuit.

out more strongly the course of events in the higher frequency range. The fact that the curves obtained with the various inductances join up where they overlap in frequency shows clearly that the *frequency* of the resonant circuit is the determining factor in the large discrepancy between observation and theory.

The points marked G in Fig. 6 were obtained with a less reliable circuit and are included merely to show that the order of magnitude, at least, of the observed ratio does not lie far from unity up to the natural frequency of 100,000 p.p.s. The solid lines E and F in the same figure are plotted, for a comparison, from Hartmann's data for a tantalum filament at the space currents of 2 milli-amperes and 20 milli-amperes.<sup>6</sup>

Even when the ratio of the observed to the calculated value of  $\bar{V}^2$  is considerably larger than unity, it is still independent of the effective damping resistance in the resonant circuit. Fig. 8 presents a series of

<sup>6</sup> C. A. Hartmann, Phys. Zeits. 23, p. 436 (1922).



observations in which the resistance  $R$  was varied from 29 ohms at the upper end of the curve to 1029 at the lower end. This last value is about half the critical damping resistance of the circuit, and yet the points lie on a straight line within the errors of measurement.

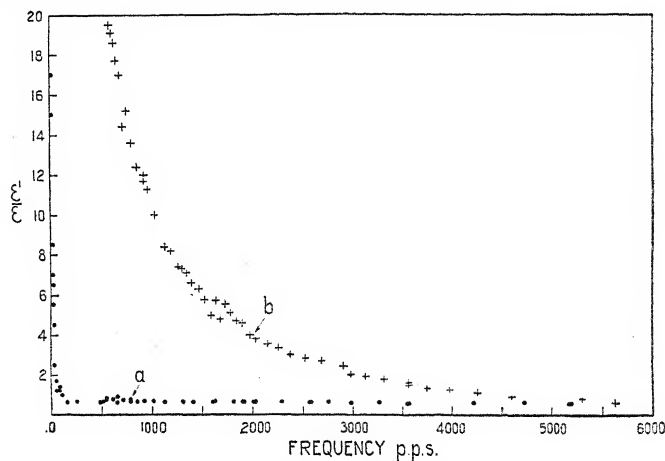


Fig. 7. Frequency variation plotted to a linear frequency scale.  
a. Tube No. 1, tungsten filament; inductance A; current 5 m-a.  
b. Tube No. 2, coated filament; inductances B and D; current 5 m-a.

The curves of Figs. 3 to 8 have to do with the dependence of the observed effect upon the circuit constants and show that except in so far

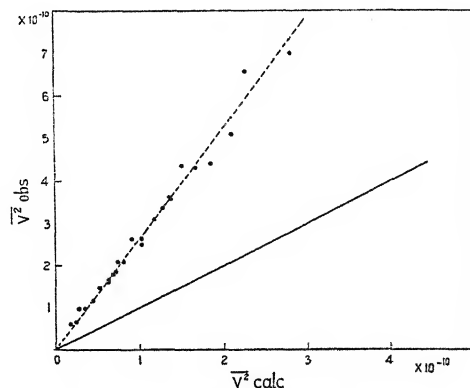


Fig. 8. Resistance variation for tube No. 3, coated filament; inductance A; capacity  $.07\mu\text{f}$ ; frequency 1900 p.p.s.; current 5 m-a.; resistance 29 to 1029 ohms.

as the circuit constants determine the *frequency* of the circuit their influence is that predicted by the theory. This fact, as well as that different tubes give different results, shows that the deviations of the observed



ratio from unity is not caused by failure of the theory to use the circuit constants correctly but by the inadequateness of the original assumptions at the basis of the theory.

Curves relating the observed and calculated voltage fluctuations as the space current is varied throw interesting light on the subject of these deviations, especially again in the case of the oxide coated filaments. Fig. 9 gives two such curves for a tungsten filament, and Fig. 10 gives a series of curves obtained with an oxide coated filament, the space current being controlled by the filament temperature. In the measurements on the tungsten filament tube the current  $i_0$  ranged from 10 milli-amperes to .01 milli-ampere, and in this thousand-fold range there is no marked deviation of the curve from linearity although the observed values are

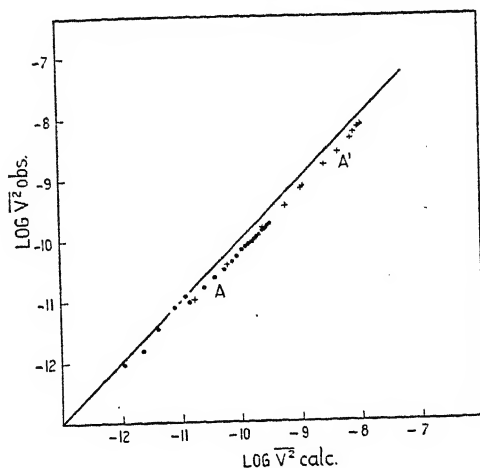


Fig. 9. Current variation for tube No. 1, tungsten filament; inductance A; capacity .10 $\mu$ f for A, .01 $\mu$ f for A<sub>1</sub>; frequency 1590 and 5300 p.p.s.; current 10 to .01 m-a.

low by about the same amount as they are in Fig. 3. Experimental obstacles prevented getting a curve at the low frequencies where, as in Fig. 3, the observed  $\bar{V}^2$  is much too high.

In the corresponding curves for the oxide coated filaments, Fig. 10, the space current range was from 5 milli-amperes down to .1 milli-ampere in most cases. The remarkable feature about these curves is that they all approach the theoretical line as the space current is decreased. It is as if with decreasing current, or perhaps decreasing filament temperature, the ideal conditions were approached which are assumed in the theory and which for the same current values more nearly exist in the tungsten cathode tubes.

## B. SCHOTTKY EFFECT AND SPACE CHARGE

The modification of the Schottky effect caused by the appearance of space charge in a two-electrode tube is shown typically in Fig. 11. For this

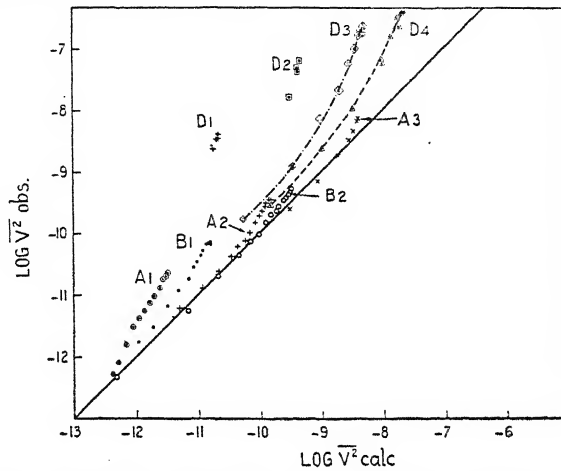


Fig. 10. Current variation for tube No. 2, coated filament; inductances as shown by letters; capacities  $A_1$ ,  $.80\mu\text{f}$ ;  $A_2$ ,  $.10\mu\text{f}$ ;  $A_3$ ,  $.010\mu\text{f}$ ;  $B_1$ ,  $.20\mu\text{f}$ ;  $B_2$ ,  $.02\mu\text{f}$ ;  $D_1$ ,  $1.00\mu\text{f}$ ;  $D_2$ ,  $.10\mu\text{f}$ ;  $D_3$ ,  $.0101\mu\text{f}$ ;  $D_4$ ,  $.0022\mu\text{f}$ ; current range 5 to  $.1$  m-a.

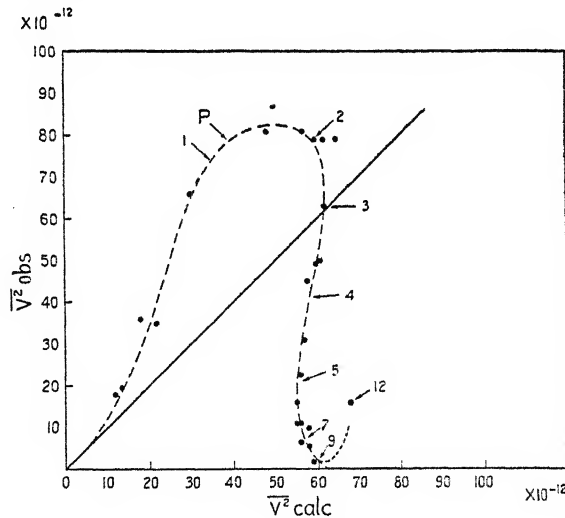


Fig. 11. Effect of space charge for tube No. 2; inductance A; capacity  $.10\mu\text{f}$ ; frequency 1590 p.p.s.; current in m-a. given by figures.

experiment the anode potential was reduced to 9 volts and the space current was controlled by the cathode temperature. The space current values, in milli-amperes, are indicated by the figures attached to the

arrows. The curve relates to tube No. 2, with oxide coated filament. As was the case with the higher anode voltage the observed values of  $\bar{V}^2$  increase faster than the calculated. At the current of one milli-ampere, however, space charge begins to be appreciable and the observed values of  $\bar{V}^2$  decrease until at 10 milli-amperes it is a small fraction of the calculated value.<sup>7</sup> Above ten milli-amperes<sup>8</sup> the observed values again increased and became very erratic, and the sound when heard in the telephone was characteristically changed.

Tungsten filament tubes show this effect of increasing noise in the space charge region to a much larger degree and at a much sharper limit. At the current value where the effect of space charge is just discernible on the space current-temperature diagram, corresponding to the point *P* in Fig. 11, current pulses begin to be superimposed on the more regular Schottky effect. These become more frequent as the filament temperature is increased until thermocouple measurements are difficult or impossible. An attempt to estimate the magnitude of these pulses was made by comparing them with the effect of discharging a small condenser through some part of the circuit. The estimates indicated that the pulses were equivalent to the passage, or the failure to pass, of a charge of  $10^5$  to  $10^8$  electrons.

If these current pulses were produced by the sudden emission, or failure of emission of a group of electrons from the filament they would, like the Schottky effect, be most distinct in the absence of space charge and would be suppressed in the space charge region. Since the opposite is the case they must be caused by something which acts upon the space charge and thereby varies the current. The evidence points to the conclusion that the "clicks" are caused either by ions which pass through the space charge or by ions which are held in the space charge region near the filament for some time. In the case of a current pulse of  $10^8$  electrons, a calculation shows that this could be produced by the passage from the filament to the plate of  $2.3 \times 10^6$  hydrogen ions, of  $1.7 \times 10^5$  singly charged tungsten atoms or of one singly charged tungsten particle  $2 \times 10^{-3}$  mm in diameter. The large size of the particle seems to rule out the last hypothesis, but there is as yet no other discriminatory evidence.

The phenomena which space charge introduces in the two-electrode tube are also present in the three-electrode tube where the current is

<sup>7</sup> The calculated value of  $\bar{V}^2$  fails to rise linearly with increasing space current because of the lowered internal resistance of the tube, which in turn greatly lowers  $R_1$ .

<sup>8</sup> The saturation current for the oxide coated filament is not well defined, and the higher currents were reached by heating the filament considerably above the normal temperature.

controlled largely by the artificial space charge of a grid. Fig. 12 contains the data obtained with the tungsten filament tube No. 1, plotted similarly to those of Fig. 11 for the two-electrode tube. The space current, denoted as before by the figures attached to the arrows, was controlled by the filament temperature. As in the case of the two-electrode tube the noise decreases with the appearance of space charge, but here only to about one-third of the theoretical value as against nearly zero for the two-electrode tube. The fluctuation which remains, however, gives rise to a sound in a telephone of the same character as does the pure Schottky effect and is no doubt a Schottky effect which is modified by the space

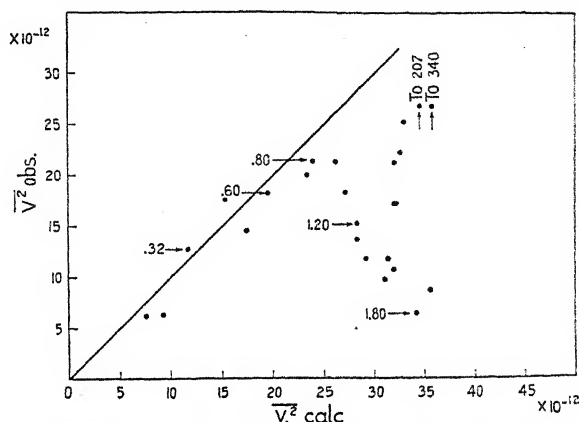


Fig. 12. Space charge in three-electrode tube No. 1; inductance A; capacity .10 $\mu$ f; current in m-a. given by figures.

charge. This conclusion seems supported by the fact that there is a relation between the noise a tube produces and the amplification as measured in the same condition, such that the ratio of noise to amplification is never less than a certain value. This is made clear by Fig. 13 in which each circle indicates in arbitrary values the measurement of noise and of amplification of one tube. A wide variety of tubes were used for this set of measurements. The circles of the diagram lie to the right of a straight line through the origin with only one or two exceptions. It seems probable that this line represents the residual of the Schottky effect in tubes when other disturbances are absent.

The inherent "noise" in vacuum tube amplifiers cannot, therefore, be estimated by the theory of the Schottky effect as it now stands. This is so partly because the theory has not been extended to take into account the presence of space charge, and still more because the remanent Schottky effect is usually masked by other disturbances which become effective when space charge appears.

## DISCUSSION

The experimental results cited here give force to the contention of Fry<sup>1</sup> that the Schottky effect is not a proper means for measuring the charge on the electron. It is rather a phenomenon which enables us, with the aid of *the already known value of  $e$* , to determine the truth or falsity of the basic assumptions underlying the theory. The assumption which has the least foundation on previously known facts, instinctive though it may be, is that which concerns the random emission of electrons, and it is to this assumption that the test of the experiments should be, and here has been, applied. The discrepancies existing between theory and experiments, with the striking introduction of the frequency as an independent vari-

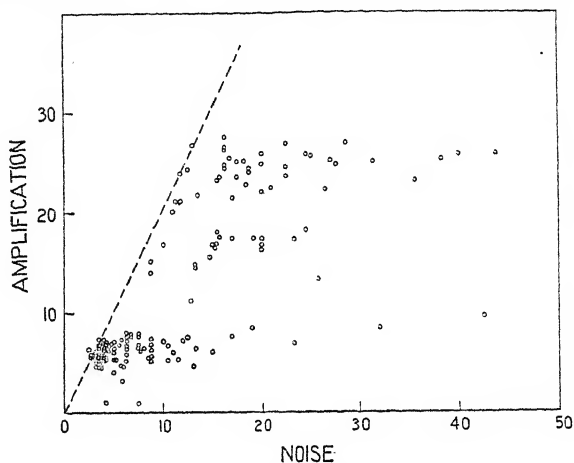


Fig. 13. Amplification as a function of noise in three-electrode tubes; noise in arbitrary units; each point represents a tube.

able, are clearly caused by the fact that the electron emission does not strictly follow the chaotic sequence assumed in the theory. However, since this deviation takes a much simpler course than Hartmann's results indicated, it yields to an explanation which seems more plausible than that offered by Hartmann and Schottky.<sup>9</sup>

The Hartmann-Schottky hypothesis is that the cooling produced on a small surface of the cathode by the emission of one electron makes the emission of another electron from the same area less probable for a time comparable with the natural period of the resonant circuit. The present data, however, do not show the maxima and minima in the  $\bar{V}^2$ -frequency curve that are so prominent in Hartmann's curves (Fig. 6). Further-

<sup>9</sup> C. A. Hartmann, *Ann. der Phys.* **65**, 51 (1921);  
W. Schottky, *Ann. der Phys.* **68**, 157 (1922).

more, although such low frequencies were attained (down to 8 p.p.s.) that the time required for the small surface cooled by the emission of one electron to reach equilibrium must be very small compared with the period of the circuit, yet even at this low frequency the ratio of the observed to the calculated quantity was rising rapidly. The above hypothesis seems, therefore, to be no longer either necessary or tenable.

An assumption of a somewhat different nature leads to conclusions which agree better with the facts. We may suppose that the chance of an electron emission is influenced not so much by previous emissions as by other factors which change irregularly with the time, chiefly the activity of the filament. The electron emission at any time depends upon the condition of the cathode surface, and the surface is probably in a continual process of change due to such causes as evaporation, diffusion, chemical action, structural rearrangements and gas ion bombardment. These changes would go on at different rates in different parts of the surface and would cover areas very large compared with that involved in the emission of one electron. The changes involving the greater area or larger amplitude might be expected to require a longer time, while changes so small as to affect only a few electrons would lose their significance in the general statistical emission. The general effect of these changes would be a variation in the total space current superimposed upon the fluctuation of the Schottky effect, having little influence at the high frequencies and an increasing effect as the natural frequency of the measuring circuit becomes lower. Again, the effect might well be greater for the composite surface of an oxide coated cathode than for one of a relatively pure metal, and the effect might be more dependent upon the temperature with a cathode of the former type.

The sum of these considerations, therefore, seems favorable to the view that the large discrepancies between theory and experiment at the lower frequencies are caused by secular changes in the surface conditions of the cathode. The values of  $\bar{V}^2$  which are too low, on the other hand, sometimes as low as one-fifth of the theoretical value, require a different explanation, but no adequate explanation has been found.

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## NON-MAGNETIC FILMS OF NICKEL

BY L. R. INGERSOLL AND S. S. DE VINNEY

## ABSTRACT

**Properties of sputtered nickel films.**—(1) *Magnetic.* These films, prepared by sputtering in hydrogen on to a cooled surface, with a 1000 volt d.c. generator, are initially non-magnetic, showing neither magneto-optic rotation nor tractive effects in a magnetic field. After heating to 300° or 400°C, however, they become strongly magnetic and exhibit both these effects. Films much thicker than 120m $\mu$ , or those sputtered with an induction coil, are likely to be magnetic from the start. (2) *Crystal structure.* X-ray spectrograms by the powder method show for the heat-treated (magnetic) film the face-centered cubic lattice as for ordinary nickel, but prove that the original non-magnetic film is amorphous. These facts suggest that *ferro-magnetism* in nickel, at any rate, is not a property of the individual atom as customarily supposed, but of the crystalline aggregate. A number of possible objections to this point of view are taken up and discussed. (3) *Electric.* The gain in magnetic properties on heat-treatment is accompanied by a decrease of *resistance* to a fraction (a fifth in one case) of its initial value. The original film also gives only about 1 percent of the *Hall effect* that it does after heat-treatment. (4) *Color.* Some films, particularly those deposited on a surface at liquid-air temperatures, display remarkable colors. On examination of the reflected light with a spectroscope, only a narrow spectral region is seen to be absent. If the nickel films are thin, covering with an optically dense liquid completely destroys the colors.

SOME years ago one of the writers noticed that most films of nickel sputtered in hydrogen showed little or no Faraday or Kerr magnetic rotation. On taking up the matter later it was found that these films which gave no magneto-optic rotation also *showed no tractive effects* when suspended in a magnetic field, although after heating to a few hundred degrees for a short time both magneto-optic and tractive effects appeared.

As this "non-magnetic nickel," if such it can be considered, has seemed of more than passing interest, and the change to the magnetic form produced by heating is so striking, considerable study has been devoted to it and the results will be described briefly.

*Preparation of films.* These were deposited with the apparatus described in a recent paper,<sup>1</sup> the chief novelty of which was the arrangement for keeping the surface (microscope cover-glass) on which the film was sputtered, cooled by running water or even liquid air. The cathode was a 32 mm disk cut from a plate of very pure nickel furnished by the International Nickel Co., through the kindness of Dr. Paul D. Merica. The

<sup>1</sup> L. R. Ingersoll, J. Opt. Soc. Amer. & R. S. I. 8, 493 (1924)



analysis was given as: nickel, 99.48 percent; cobalt, 0.40 percent; iron, 0.10 percent; copper, 0.02 percent.

While an induction coil was used in some cases, the fifty or more best films were deposited with a direct-current generator at about 900 to 1000 volts. The cathode was 15 to 18 mm from the glass and the vacuum such that the dark space extended almost to its surface, the current being 15 to 20 milliamp. Save for a few experiments with nitrogen, the residual gas in all cases was hydrogen.

*Magnetic tests* were admittedly very primitive but quite satisfactory for the purpose. After sputtering, the film was cut into strips about  $5 \times 25$  mm and one of these was suspended by a thread so as to swing freely between the poles of an electromagnet giving a field of some 12,000 gauss. The tractive effects when the current was turned on were observed and estimated on a scale of 1 to 100, the former representing the smallest observable motion and the latter about the magnitude one would expect for ordinary nickel; that is, an effect such that the film would instantly be drawn to one of the pole pieces. In making these estimates account had to be taken of the width and relative thickness of the film, factors which would make really accurate measurement a difficult problem.

*Heat treatment* was carried on at various temperatures between  $100^\circ$  and  $450^\circ\text{C}$  or higher, generally in a fairly good vacuum or low pressure (0.1 mm) hydrogen, although a few tests in hydrogen at atmospheric pressure and also in hot oil gave essentially the same results. The time element is quite secondary to temperature; a few minutes at  $400^\circ$  were much more effective than hours at  $250^\circ$ , while a few seconds in a Bunsen flame in air produced a large effect, although this was not easily controllable. A number of nickel films were sputtered over with a layer of gold and then heated. The surface then generally showed little blisters, indicating that the heat treatment involved an escape of gas (hydrogen) as would be expected. Some experiments were also tried on alloying with gold by sputtering this metal along with the nickel from a small strip across the cathode. The general characteristics were the same save that the gaining of magnetic properties upon heating was somewhat slower and not so marked. No substitute for heating, for bringing about magnetic properties, has been found. Ageing in a dessicator for six months or more produced little if any effect. Tests on ageing in a vacuum are not yet conclusive—3 months in vacuum seem to yield no results—although some effect might well be expected here from the experiments of Koller<sup>2</sup> on ageing platinum films in a vacuum. A trial of burnishing with a

<sup>2</sup> L. R. Koller, Phys. Rev. 18, 221 (1921).



rounded glass rod, which might be expected to compact anything like a loose powder, brought about no magnetic effect.

*Resistance measurements.* The work of<sup>3</sup> Richtmyer and others shows that the resistance of a sputtered film generally decreases rapidly upon heating, so a like effect was to be expected for these nickel films. A test of a film the ends of which had been sputtered with gold to insure good contact, gave the following results:

Heat treatment	Resistance	Magnetic intensity
Original film	30.6 ohms	0
17 hr at 100°C	26.8	2
19 hr further at 150°	24.1	4
18 hr further at 200°	19.4	12
4 hr further at 250°	16.7	16
1.5 hr further at 300°	16.6	25
0.5 hr further at 350°	10.6	50
0.1 hr further at 400°	7.0	60
0.5 hr further at 450°	6.0	80

Other films showed qualitatively the same effects. If the heating at the higher temperatures was prolonged the film began to crack and the resistance rose. The change in resistance and in magnetic properties of the film tabulated above was probably almost complete.

*Crystal structure.* The powder method (G. E. apparatus, molybdenum tube) was used. The film was scraped from the glass with a sharp knife—it was usually strongly adherent and the scrapings resembled a fine black powder—and packed into the capillary tube. This was then tested in the magnetic field and showed no tractive effects. A 12 to 24 hr exposure was then made on it, after which it was heated to 400° for a short time and another exposure made. It was strongly magnetic after heating. Check films were also made on filings of metallic nickel and on a blank glass tube. The comparison substance in all cases was aluminum.

The photographs for the nickel filings and *heat-treated film* were practically identical and showed the face-centered cubic lattice as found by Hull<sup>4</sup> for this metal. *The original untreated nickel film, however, showed an amorphous character.* A second test, in which the nickel films used were especially carefully selected for their absence of any magnetic tractive effects, gave particularly conclusive evidence on this point.<sup>5</sup> Only the line produced by the (111) planes was present, indicating the presence of small groups containing only a few molecules each—not enough to produce interference of a higher order.

<sup>3</sup> F. K. Richtmyer and L. F. Curtiss, Phys. Rev. **15**, 465 (1920); L. F. Curtiss, Phys. Rev. **18**, 255 (1921); L. R. Koller, loc. cit.,<sup>2</sup> and others. See also F. W. Reynolds, Phys. Rev. **24**, 523 (1924).

<sup>4</sup> A. W. Hull, Phys. Rev. **17**, 571 (1921).

<sup>5</sup> Dr. Hull, who obligingly examined the x-ray films, considers that they prove beyond question that these nickel films are amorphous.

*Other experiments.* The films were ordinarily deposited in about half an hour and were usually almost opaque. Measurements by the interference method on an average film gave a thickness of about 120m $\mu$ . When the thickness was greatly in excess of this the film generally showed some magnetic properties from the start. In one case when the sputtering was continued for 20 hr the film was apparently as magnetic as ordinary nickel. This indicates that it would be difficult, if not impossible, to obtain this amorphous nickel in bulk form.

A number of films were sputtered with an induction coil, with varying results as regards magnetic characteristics. The rule seemed to be that the higher the potential used in sputtering the more likely the film was to turn out somewhat magnetic. A few films were sputtered in nitrogen but the results were unsatisfactory. The idea gained, on very little evidence, however, was that films deposited in this gas were likely to be magnetic.

Professor Alpheus W. Smith, who obligingly tested samples of both treated and untreated films for the Hall effect, reports that, while the measurements he was able to make left much to be desired in the way of accuracy, the indications were that the original film showed hardly more than 1 percent as much effect as the heat-treated one.

*Color effects. Microscopic structure.* In many cases, particularly when the surface on which the film was sputtered was kept at liquid-air temperatures, brilliant surface colors appeared. On examining the reflected light with a spectroscope it was found that only a narrow spectral region was absent, and that this absorption band moved towards the red with increasing film thickness. This duplicates almost exactly the observations of Wood<sup>6</sup> on sodium and potassium films. It is possible, however, to try certain things with nickel films which cannot be done with sodium and potassium and one of these is to cover with water or other liquid. It was found on trying this that, with thin films, liquids of low refractive index such as water dulled the color, while optically denser liquids like carbon bisulphide or mono-bromnaphthaline completely destroyed it, although the color returned when the liquid was washed off. This might be construed in favor of Wood's theory that this absorption is a type of resonance phenomenon taking place in the interstices between the particles.

The matter of film color, however, is far from simple. In the thicker films the effect of the liquid was not as definite as explained above. Such films also occasionally showed evidence under the microscope of being double or triple in character after heat-treatment. In general an original film showed no trace of structure, while a heat-treated one frequently

<sup>6</sup> Phil. Mag. 38, 105 (1919)

showed a very complicated structure when examined with oil-immersion objective, although no connection could be clearly traced between this and the color effects. The colors were almost invariably changed by heating, sometimes disappearing and sometimes appearing when they did not exist before.

#### DISCUSSION OF RESULTS; CONCLUSIONS

Undoubtedly the most important conclusion to be drawn from this work is that, on the evidence of these films, *ferromagnetism in nickel requires a crystalline structure and is therefore not a property of the individual atom, but of the crystalline aggregate*. Whether or not this means that the Amperian currents must circulate in orbits wider than the ones of atomic size customarily supposed, becomes a matter of interpretation, but the evidence would certainly seem to point in this direction.

There is a possible escape from this conclusion that the original film is non-magnetic because amorphous. As already mentioned, scrapings from such a film resemble a fine black powder. If this film, as originally deposited, could be regarded as a loose aggregate, its lack of magnetic properties might then be at least partially attributed to this fact rather than to its amorphous character. There are several reasons which have caused this point of view to be rejected: (a) The original film is tough and resistant, hard to rub off or scrape off. (b) Its optical properties are not at all such as one would associate with a loose powder. In appearance the film is bright and metallic-looking. The change produced by heating is small; it is slightly darker afterwards and has a faint golden tinge. (c) Its electrical resistance, while lessened by heat-treatment, is not high and indicates a coherent metal structure. Moreover, it cannot be assumed that the film is a compressed, rather than a loose powder, since the work of Speed and Elmen<sup>7</sup> on the magnetic properties of compressed powdered iron show a value of the permeability up to several hundred for this material.

Another possible suggestion, namely that the nickel as originally sputtered might be in an oxidized state and that the heat-treatment—usually carried out in hydrogen—involved a reduction of this to metallic nickel, may be answered at once by pointing out that heat-treatment could be effectively carried out in the oxidizing part of a Bunsen flame. Furthermore, great care was taken to secure pure hydrogen for sputtering and the slightest air leak always meant a ruined film.

The fact that there was apparently an escape of hydrogen during the heating process is not taken to have any particular significance. It is true

<sup>7</sup> Speed and Elmen, Trans. Am. Inst. Elect. Engineers, 40, 1321 (1921).

that occluded hydrogen modifies<sup>8</sup> somewhat fundamentally the magnetic characteristics of some metals. But it is hard to see how this fact can be used to explain the non-magnetic character of these nickel films, when, as already stated, thicker ones, or, for that matter, films deposited with an induction coil, may turn out strongly magnetic.

The absence of Hall effect in the unheated films is not unreasonable in view of their amorphous character. The fact that they show no magneto-optic rotation, however, is probably a purely magnetic phenomenon and due to the lack of high internal magnetic fields in the non-magnetic specimen.

While no evaporated films have been tested as yet in connection with the present experiments, one of the writers found, a few years ago, that evaporated nickel films showed magneto-optic rotation. This doubtless means that such films are ordinarily magnetic<sup>9</sup> and therefore crystalline, as was found by Steinberg<sup>10</sup> to be the case for evaporated silver and iron.

In conclusion, the writers accept the common view of the sputtered film as an aggregate which is brought into a greater degree of coalescence by heating. As the present work shows, this aggregate may be initially amorphous in some cases, if temperature and voltage conditions during deposition are properly controlled. Whether the sputtered particles are single atoms, as assumed by some investigators, or actual granular crystals, as believed by Kahler,<sup>11</sup> is a much-discussed question on which this work perhaps throws a little light. For the amorphous film must be built up either of single atoms or of exceedingly small groups, while, on the other hand, the apparent effect of higher voltages in producing crystalline films would be in accord with the view of such voltages giving larger sputtered particles, crystalline in character—although, of course, there are other possible explanations, such as local heating accompanying the higher voltage.

Cobalt and iron films are now being investigated to see to what extent they bear out these conclusions for nickel, particularly as regards the connection between magnetization and crystal structure.

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PHYSICAL LABORATORY,  
UNIVERSITY OF WISCONSIN,  
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<sup>8</sup> A. E. Oxley, *Proc. Roy. Soc.* **101**, 264 (1922).

<sup>9</sup> On this point see A. J. Sorensen, *Phys. Rev.* **24**, 658 (1924).

<sup>10</sup> J. C. Steinberg, *Phys. Rev.* **21**, 22 (1923).

<sup>11</sup> H. Kahler, *Phys. Rev.* **18**, 216 (1921).

# ON ELECTRIC CHARGES CARRIED BY INDIVIDUAL MICROSCOPIC PARTICLES\*

By TH. SEXL

## ABSTRACT

Criticism of conclusions as to the existence of an elementary electronic charge, from experiments of Derieux with mercury droplets.—In these experiments observations of the same droplet were made at different pressures. The size of one droplet which apparently was constant in mass and not disturbed by air currents, is computed and a result obtained different from that obtained by Millikan's method of computation. The charges computed by using the size so determined are not multiples of a unit charge. This confirms Ehrenhaft's conclusion that other electric charges are stable on microscopic and submicroscopic metallic particles than those stable on particles of dielectrics.

(A reply by J. B. Derieux follows this article.—Ed.)

F. EHREHAFT<sup>1</sup> and his pupils working with particles of precious metals (silver, platinum, gold and mercury) suspended in inert gases (N, Ar etc.), found on them electric charges down to  $10^{-12}$  electrostatic units. This led him to the conclusion that the existence of an elementary charge is not yet proved by experiment.

R. A. Millikan<sup>2</sup> and his pupils on the other hand are of the opinion that they have succeeded in proving that all static charges both on insulators, such as oil (Millikan) and shellac (Lee<sup>3</sup>), and on conductors, e. g. mercury (Derieux<sup>4</sup>) are built up of elementary charges.

Two very strong objections, however, may be urged against the method used by R. A. Millikan and his pupils. The first is that all measurements are made on big droplets, their radii being always greater than  $3 \times 10^{-5}$  cm. The second is that these authors a priori presuppose an equality of charges on all test particles, i.e. the existence of an elementary charge, in determining the size of the charged particles, which is

\* Contrary to the general editorial policy of the Physical Review, this criticism is published in spite of the fact that it is believed to be erroneous, because of the importance of the subject, and because it was submitted by Professor F. Ehrenhaft. A reply by J. B. Derieux and a discussion by R. A. Millikan follow this criticism.—G. S. F.

<sup>1</sup> F. Ehrenhaft, Anz. Wiener Akademie, March 4, 1909; April 21, 1910; May 12, 1910; Wien. Ber. 119, 882 (1910); Phys. Zeits. 11, 940 (1910); Ann. der Phys. 44, 657 (1914); 56, 1, (1918); 63, 773 (1920).

<sup>2</sup> R. A. Millikan, Phys. Zeits. 11, 1097 (1910); Phys. Rev. 32, 349 (1911); Phys. Zeits. 14, 736 (1913); Phil. Mag. 34, 1 (1917).

<sup>3</sup> I. Y. Lee, Phys. Rev. 4, 420 (1914).

<sup>4</sup> J. B. Derieux, Phys. Rev. 11, 203 (1918).

the essential element of the droplet method. In the following a method will be put forward by which the radius of a particle is determined without any assumption of the existence of an elementary charge.

The Stokes-Cunningham law of motion

$$(4/3)a^3\pi(\sigma-\rho)g=6\pi\mu av_f(1+Al/a)^{-1}$$

can be written in the form  $a+\beta l=v_f$  if  $(2/9)(\sigma-\rho)ga^2/\mu\equiv a$  and  $(2/9)(\sigma-\rho)gaA/\mu\equiv\beta$ . It postulates a linear relationship between  $v_f$  and  $l$ . Since it is possible to measure the speed of fall of the same particle at various gas-pressures<sup>5</sup> the individual straight line is fixed by means of  $a=(v_1l_2-v_2l_1)/(l_2-l_1)$  and  $\beta=(v_2-v_1)/(l_2-l_1)$ , which quantities can be determined experimentally. If all assumptions hold<sup>6</sup>, we can compute the radius of the particle from the equation

$$a=\sqrt{(9/2)\mu a/(\sigma-\rho)g}.$$

This method of determining the size of the carrier of the electric charge is independent of every assumption about its charge.<sup>7</sup>

Now a pupil of R. A. Millikan, J. B. Derieux, has succeeded in measuring the same mercury droplet at varying gas pressures. But he did not use the above-mentioned method of calculating the radius of the droplet without recourse to assumptions about an elementary charge. Therefore by calculating the radii also according to this method, it is possible to examine R. A. Millikan's method which was used by J. B. Derieux for the determination of the radii of his particles.

On considering the data given by Derieux we find at first sight the astonishing fact that among eleven mercury-droplets (record numbers 51-61) which could be measured at varying gas-pressures, there are three for which the times of fall are longer at reduced pressures than at atmospheric pressure. Such a behavior seems at first to be unintelligible. For a more detailed discussion we plotted the reciprocals of the times of fall (speeds of fall, since distance of fall is 1 cm) as ordinates against the mean free paths  $l$  as abscissas. Through every pair of points belonging to one particle straight lines were drawn. The diagrams thus found are analogous to those already given by R. Baer.<sup>8</sup> Subsequently the radius and the density of these particles were computed according to the method used by R. Baer. For this computation the value of the constant

<sup>5</sup> First stated by E. Meyer and W. Gerlach, *Ann. der Phys.* **47**, 224 (1915) and I. Parankiewicz, *Phys. Zeits.* **19**, 280 (1918).

<sup>6</sup> (a) Sphericity of the test particles; (b) validity of the Stokes-Cunningham law with a constant  $A$ ; (c) density of the particles equal to that of the material in bulk.

<sup>7</sup> Compare *Zeits. f. Phys.* **16**, 34 (1923).

<sup>8</sup> R. Baer, *Ann. der Phys.* **59**, 394-403 (1919).



$A = 0.708$ , given by R. A. Millikan for mercury-air, was assumed. The following values were found

Drop No. :	53	55	56	57	58	59	60	61
$a(10^{-5} \text{ cm})$ :	72.73	15.59	24.37	14.44	5.149	5.805	4.213	5.051
$\sigma(\text{g cm}^{-2})$ :	1.233	1.718	0.961	2.623	11.19	9.719	20.54	19.53

In analogy to R. Baer's criticism<sup>8</sup> of Ehrenhaft's results, it would seem possible to conclude that the mercury-droplets observed by Derieux and used as evidence for the existence of an elementary charge by R. A. Millikan are either non-spherical or are of spongy structure. Such a conclusion is, however, absurd since the particles were produced by condensing the vapor of boiling mercury. We therefore must try to find a more plausible explanation for this curious behavior. Now the air in the condenser was pumped off through six holes in the center of the upper plate only, so it could happen that equilibrium between the air in the condenser and the air in the pressure-cylinder<sup>9</sup> was not reached when the time-measurements began. Therefore a rising current of air could have remained in the condenser. The result of this would be that the observed values of  $v_f$  would be found too low. Since an approximately constant current in the condenser would not influence the values of  $v_1 + v_s$ ,<sup>10</sup> these values were plotted as ordinates against the mean free paths  $l$  as abscissas. It appeared that all the straight lines which were drawn through related points showed a uniform upward direction, with a few curves crossing the others. The reason for this could not be found, because the particles are not recorded in detail (detailed records are given only for droplets No. 59 and 60).<sup>11</sup>

The criterion for proving the absence of a current or another disturbance of the measurements is to be found in the constancy of the balancing-potential<sup>12</sup> which can be computed separately for the different pressures (from the equation  $f^* = ([v_f/(v_f + v_s)]f)$ ). The detailed recorded measurements of the droplets No. 59 and 60 were examined with regard to this condition. We find

Drop No.:	59	60
Pressure in mm Hg:	750.9   348.1   196.3	751.0   430.7   299.5   180.0
$f^*,^{13}$	3.346   3.128   3.016	4.702   4.731   4.721   4.672

<sup>9</sup> Compare J. B. Derieux, l.c.<sup>4</sup> p. 205.

<sup>10</sup> Computed from the recorded radii of the particles by means of the equation  $(4/3)a^3\pi(\sigma - \rho)g = ef^*$ .

<sup>11</sup> Perhaps the evaporation of the droplets which according to J. B. Derieux is greater at reduced pressures accounts for the deviation.

<sup>12</sup> R. Baer, Ann. der Phys. 67, 182, 1922. By balancing-potential that potential is understood at which the weight of the drop is balanced by the electric field. The above-mentioned formula follows from the equations  $ef^* = mg$ ,  $mg = v_f/B$  and  $ef - mg = v_s/B$  ( $f$  = field-strength in the condenser.)

<sup>13</sup> Computed for the charge which Derieux considers as built up of four elementary charges.



For droplet No. 59 there results a maximum fluctuation of ten percent against only one percent for droplet No. 60. If we compute the mean errors of the balancing-potentials in the usual way we find an error of one percent at most. Consequently, the fluctuations for droplet No. 59 fall beyond the limits of error, which means the presence of a disturbance (current in the condenser, inconstancy of the mass of the droplet caused by gradual evaporation etc.). On the other hand, the fluctuations of the balancing-potential for droplet No. 60 lie within the limits of error and therefore the measurements can be taken as free from disturbances (no current in the condenser, constancy of the mass of the particle). Having thus gained an opinion about the trustworthiness of the measurements we can determine the size of these droplets.

By plotting their times of fall as ordinates against the mean free paths as abscissas it is shown that the linear relationship between  $v_f$  and  $l$  postulated by the Stokes-Cunningham law exists indeed. Therefore  $\alpha$  and  $\beta$  belonging to each of the straight lines were computed by means of the method of least squares. It is seen from the equation  $ef - mg = 6\pi\mu av_s(1 + Al/a)^{-1}$  or  $\alpha' + \beta'l = v_s$ , that a linear relation must also exist between  $v_s$  and  $l$ . It should be  $\beta'/\alpha' = \beta/\alpha = A/a = c$ .  $\alpha'$  and  $\beta'$  were computed in the same way as  $\alpha$  and  $\beta$ . But the batteries ran down and a little current might after all have been in the condenser. To eliminate these small sources of error  $\alpha''$  and  $\beta''$  belonging to the values of  $(v_f + v_s)/f$ , not touched by these sources of error, were computed by means of the method of least squares. It was found<sup>14</sup>

	$v_f$	$v_s$	$(v_f + v_s)/f$	$v_f$	$v_s$	$(v_f + v_s)/f$
Droplet No. :	59			60		
$(\beta/\alpha)10^{-3}$ :	147.3	239.6	220.4	165.1	167.9	171.2
$a \times 10^8$ :	4.794	4.481	4.671	5.196	5.184	5.169
$e \times 10^{10}$ :	4.588	3.962	4.243	4.156	4.124	4.091
$A$ :	0.706	1.074	1.029	0.858	0.871	0.885
$\alpha(\text{Derieux})$ :			4.815			5.445
$A(\text{Derieux})$ :			0.832			0.803

The non-agreement of the values of  $\beta/a$  gained for droplet No. 59 shows once more the presence of a source of error, as already inferred from the inconsistency of the balancing-potential.<sup>15</sup> The fluctuations of the values of  $\beta/a$  for droplet No. 60, however, lie within the limits of error,

<sup>14</sup> It should be mentioned that the electric charges measured on these big droplets are as follows: particle No. 59: 8.471; 12.717; 16.970  $\times 10^{-10}$ ; particle No. 60: 12.310; 16.624; 20.795; 25.110  $\times 10^{-10}$  electrostatic units. The exact multiples of the electronic charge would be: 9.548; 14.322; 19.096; 23.870; 28.644  $\times 10^{-10}$  electrostatic units.

<sup>15</sup> Nevertheless, the radius computed from the values of  $(v_f + v_s)/f$  cannot be in error of more than one percent under the assumption that it is essentially a current that produces the disturbance of the measurements.

as it can be shown, and the radius computed from the values of  $v_f$  cannot be in error by more than one half percent.

Thus we find that the radii of the droplets computed by us by means of a method free from assumptions about an elementary charge, and the radii computed by Derieux according to the method of R. A. Millikan from the equation  $mg = ef^*$  differ by more than four percent. Therefore the electric charges carried by these mercury-droplets show deviations of more than 14 percent<sup>16</sup> from the electronic charge and its multiples.

These deviations are in agreement with those observed by Ishida<sup>17</sup> on oil-drops and Silvey<sup>18</sup> on mercury-droplets.

To sum up it could be shown that all the measurements taken by Derieux at different gas-pressures were disturbed by causes that, however, could not be found, because the particles are not recorded in detail. Only the measurements taken on particle No. 60 could be shown to be free from these disturbances (no current in the condenser, no evaporation of the droplet). Therefore a value for the constant  $A$  could be computed from the measurements on this particle. The value of the constant  $A$  was found to be 0.858 against the value 0.708 given by Millikan. The sphericity of the particles being beyond doubt, the only assumption for this computation is that the density of the particle is equal to that of the material in bulk. On the other hand the assumption of a constant  $A = 0.708$  would mean a density of this mercury droplet  $\sigma = 21.2$ .

As it is well-known, R. A. Millikan always brought forward the paper of J. B. Derieux as a proof<sup>19</sup> for the theory that all electric charges carried by mercury-droplets are of the same value ( $4.774 \times 10^{-10}$  e.s.u.) as those carried by insulators. The present investigation shows the fallacy of this argument.

PHYSICAL INSTITUTE,  
UNIVERSITY OF VIENNA,  
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<sup>16</sup> At least ten percent of this lies beyond the limits of error.

<sup>17</sup> Y. Ishida, *Phys. Rev.* **21**, 561 (1923).

<sup>18</sup> O. W. Silvey, *Phys. Rev.* **7**, 102 (1916).

<sup>19</sup> R. A. Millikan, *Phys. Rev.* **8**, 620 (1916); "The Electron," p. 176, 1917.

REPLY TO TH. SEXL'S CRITICISM OF R. A. MILLIKAN'S  
METHOD OF COMPUTATION OF THE ELEMENTARY  
ELECTRICAL CHARGE ON MERCURY DROPLETS

BY J. B. DERIEUX

## ABSTRACT

It is shown that Sexl's test method is in error because it is based upon the assumption that the droplets remain of the same size throughout the observations. Data are given which prove that because of evaporation such is not the case. Errors, also, are shown in his computations, which, when corrected give results approximating those by the Millikan method, with the difference in favor of the Millikan method.

THE method suggested by Th. Sexl<sup>1</sup> for testing Millikan's method of computing the elementary electrical charge, by using the writer's results<sup>2</sup> at varying pressures, assumes that the radius of a droplet remains constant through varying pressures. That this is certainly not true, is beautifully demonstrated by the three droplets which Sexl discarded as being unintelligible. They had evaporated so much by the time the observations at reduced pressure were reached that their times of fall under gravity were less than at atmospheric pressure. These droplets showed excessive rates of evaporation at atmospheric pressure, and this continued at reduced pressure. Therefore it is most certain that the evaporation did not cease during the intervening period, and then start again. Number 52 was the most striking one. Its mean times of fall at atmospheric and reduced pressures were 12.54 and 18.44 sec., respectively. At atmospheric pressure it started at 12.10 sec. and evaporated to 13.36 sec.; at reduced pressure it was reduced from 17.60 to 19.20 sec. The periods of observation were about 20 and 15 min., respectively, while the intervening period was considerably longer than either, for I evacuated very gently so as not to disturb the remaining air very much, and then I waited until I was confident that any air currents had ceased. Therefore it cannot be doubted that the increase in time of fall at reduced pressure over that at atmospheric pressure is the result of evaporation during the intervening period. The other two droplets present similar evidence.

With these three droplets most certainly demonstrating the smaller size at reduced pressure, it is evident that it is erroneous to assume no change. No droplet can be treated as the same droplet at two pressures, but must at each pressure be considered as a separate and distinct one. This is just what I did in all the work which is here under discussion, as may be seen from my original paper<sup>2</sup> in which I not only stated this fact

<sup>1</sup> Th. Sexl, preceding paper.

<sup>2</sup> J. B. Derieux, *Phys. Rev.* **11**, 203 (1918)

clearly but recorded different radii for all my drops at different pressures. With No. 52, just referred to, for example, I recorded its radii as  $6.604 \times 10^{-5}$  cm at atmospheric pressure, and 5.163 at reduced pressure. And yet Sexl deliberately ignores all this and assumes the same radius for all pressures. Hence, obviously, the error of his results.

However, I did not understand why the results by his method should be as much in error as his published values, and so I computed the radii by his method, taking

$$a^2 = 9\mu(v_1 l_2 - v_2 l_1) / 2(\sigma - \rho)(l_2 - l_1).$$

It was expected that the results by his method would be too large, for evaporation had so reduced the sizes of the droplets that  $v_2$  was too small. Below are the results of my computation by Sexl's method given in comparison with those by Millikan's method. It is evident that Sexl had made inexplicable errors in his computations or has used incorrect values of his constants for his results do not agree with the ones which I obtain by his method.

Drop number:	53	55	56	57	58	59	60	61
By Sexl's method (my calc.):	6.98	5.51	6.36	6.39	4.68	4.83	5.23	6.03
By Millikan's method:	6.83	5.38	6.15	6.12	4.76	4.81	5.38*	6.07

They agree as well as could be expected, and the difference is in favor of Millikan's method, which gives the smaller value, as predicted, for the droplets which show reduction in size by evaporation. His values for Nos. 58, 60, and 61 are larger than those by the other method, which appears unfavorable at first thought, but these droplets show an increase in size during observation, and, consequently, Sexl's method would give values too small for them.<sup>3</sup>

The balancing potentials, contrary to his statement, are not constant, but show a decided decrease in droplets which show a reduction in size, as may be noticed from his values—3.346, 3.128, and 3.016—for No. 59. This gives further evidence of a reduction in size of the droplets.

The fact that the fluctuations in the results from No. 59 are greater than those from No. 60, which fact Sexl makes use of, is easily to be accounted for by evaporation of No. 59.

The conclusion is that Sexl's criticism of Millikan's method has no foundation, being based upon a wrong assumption.

WILLIAM KEARNEY CARR PHYSICAL LABORATORY,  
NORTH CAROLINA STATE COLLEGE,  
RALEIGH, N. C.  
February 1925.

\* In the original paper, by an error in calculation, 5.44 was given instead of 5.38, and on p. 222, by typographical error, 5.29 was given for 5.39.

<sup>3</sup> J. B. Derieux, *l.c.*,<sup>2</sup> pp. 223-224.

THE NATURE OF THE EVIDENCE FOR THE  
DIVISIBILITY OF THE ELECTRON

BY R. A. MILLIKAN

## ABSTRACT

The purpose of this note is to remove misconceptions due to erroneous statements regarding the determination of the elementary electronic charge by the oil-drop method. It is emphasized that the existence of an elemental charge is directly proved by the multiple relationship shown to exist between successive charges on each test particle; that the unitary character of electricity is not presupposed even in determining the absolute value; and that the method used by Sexl in determining the radius of the droplet is not essentially new. Recent photo-electric work of Hake and of Wasser is discussed briefly.

FOR the past eight years I have taken no part in the discussion of the nature of the evidence for the divisibility of the electron, since it has seemed to me that the published data told the story quite plainly to any one who would take the trouble to examine them critically. Further, I stated the case as clearly as I could in 1916<sup>1</sup> and no evidence has appeared since to modify the conclusions then drawn, or, indeed even to need further discussion, save only the very recent photo-electric work of Hake<sup>2</sup> and of Wasser,<sup>3</sup> which will be touched upon below.

I believe that every one of the observers outside of Vienna who has repeated my work has both checked my experimental results and reasserted my conclusions upon all the essential points in dispute,<sup>4</sup> while even in Professor Ehrenhaft's laboratory itself one observer, Schmid,<sup>5</sup> has found, like all the rest of us, that measurements upon the Brownian movements of minute suspended particles in air do not lead, as formerly asserted in Vienna, to too low a value of  $Ne$ , while another observer, Mattuck,<sup>6</sup> has found by using my oil-drop method without any essential modification, that my results, both as to the complete law of fall of a spherical particle and as to the uniform appearance upon all particles, little and big, of the charge of about  $4.7 \times 10^{-10}$  electrostatic units, were correct within the limits of his rather large experimental error.

<sup>1</sup> Millikan, *Phys. Rev.* **8**, 595-625 (1916).

<sup>2</sup> Hake, *Zeits. f. Phys.* **15**, 110 (1923).

<sup>3</sup> Wasser, *Zeits. f. Phys.* **27**, 226 (1924).

<sup>4</sup> See Bär, *Ann. der Phys.* **67**, 157 (1922); also *Die Naturwissenschaften* **14** and **15**, 1922.

<sup>5</sup> Schmid, *Zeits. f. Phys.* **5**, 31 (1921).

<sup>6</sup> Mattuck, *Phys. Zeits.* Dec. 1, 1924, p. 620.

Scarcely any further extensive discussion of the sub-electron problem then seems necessary now, but it is perhaps worth while to correct, for the benefit of those who have not the time to study the original data, some fundamental misconceptions which may have been gained from erroneous statements which have been repeatedly made in the course of this discussion and which are reasserted by Sexl.

1. *Nothing could be more fundamentally incorrect than the statement that my method presupposes an equality of charge on all test particles, i. e., the existence of an elemental charge.* It is altogether obvious that no assumption whatever regarding the character of the charge  $e$  on the droplet is involved in my fundamental equation

$$\frac{v_1}{v_2} = \frac{mg}{Fe - mg}$$

or

$$e = (mg/Fv_1)(v_1 + v_2) = K(v_1 + v_2).$$

This equation shows that the charge  $e$  on the drop, whatever its value, is proportional to the velocity communicated to the drop, namely  $(v_1 + v_2)$  by the constant field  $F$  acting on the charge  $e$ . In other words, this charge  $e$  is measured in my method in terms of the speed  $(v_1 + v_2)$ . The essence of the method consists in *changing* the charge and hence  $v_2$  by capturing ions, by photo-electric discharge, by x-rays,  $\alpha$ ,  $\beta$  and  $\gamma$  rays, etc., and in finding by such change all the values of  $(v_1 + v_2)$  that can be obtained. The atomic nature of electricity is revealed conclusively in the experimental fact that this series of possible speeds is actually found to bear the relations 1, 2, 3, 4, 5. *It is in this purely experimental multiple relationship in the speeds of drops all of which capture the same sort of ions from the air that the proof of the atomic theory of electricity rests, and it is at this point that the attack on the atomic theory of electricity must be made if it is to be worthy of any serious consideration whatever.*

Now, so far as I know, no one has ever published any data that are susceptible of careful analysis for this multiple relationship and that yet fail to reveal it. Further, no data should be considered as evidence in which the charge upon a given drop is not changed enough times to test thoroughly the existence or non-existence of this multiple relationship. In so far as I can see from the rather meager data that Hake and Wasser publish in their recent photo-electric work, their drops do show this unitary progression of charge, and if they do then it may be taken as practically certain that these gentlemen are not dealing with sub-electrons, for I have demonstrated conclusively that the charges caught from ionized air, such as some of the observed charges will always be if



the observations are long continued, are uniformly electrons, and I think it is not too much to assert that they must be electrons in Vienna if they are such in Pasadena and Chicago.

It is true that I do not yet understand fully what Wasser calls his "inverse photo-electric effect," but it seems to me likely that he obtains this effect by catching electrons released from the surrounding walls by ultraviolet light instead of by detaching positive charges from his droplet by ultraviolet light, as he thinks that he does. But this point can be tested easily, and we are in the process of making this test in this laboratory. By changing the charge on a given drop, first with the aid of ultraviolet light and then by throwing upon it ions produced by the passage of a beam of x-rays underneath the drop, it will be possible to observe directly whether these two changes in charge produce the same change in speed. The question of the appearance of the sub-electron in these experiments can then be settled definitely without making any assumptions whatsoever about the densities of the drops worked with.

2. *It is fundamentally erroneous to suppose that even in the reduction of the value of the electron from velocity units to absolute electrostatic units—an operation which does presuppose the density and sphericity of the droplet—any presupposition whatever as to the unitary character of electricity is involved.* A glance at any of my early papers upon this subject will show that the radius  $a$  of the drop was determined entirely from Stokes' law—or from a slightly corrected form of Stokes' law—and involves no suppositions of any kind as to the nature of the electrical charge. The two-thirds' power of the smallest charge (measured in terms of a speed) *that the drop actually carried*—this smallest charge could be unerringly computed from the observed multiple relationship in speeds, but not even this computation was necessary since plenty of drops could be obtained upon which it was *directly observed*—was plotted against  $1/pa$ ,  $a$  being computed from Stokes' law, viz:  $mg = 6\pi\mu av_1$ . This plotting yielded a single straight line. It is quite true that it could not have done this unless all of the drops, when most lightly charged, carried one and the same unit charge, as the multiple relationship had already shown that they did, *but the straight line, like the multiple relationship, is an experimental fact from which the unitary character of the charge follows. It is not an assumption.* The absolute value, too, of the electron was now approximately determined by the intercept of the straight line on the  $e_1^{2/3}$  axis. This line also yielded, through its slope, the approximately correct value of the first correction term,  $A$ , to Stokes' law, which thus became  $mg = 6\pi\mu av_1(1 + A/a)^{-1}$ . This new equation, with  $A$  now approximately known, was then solved to obtain a final value for  $a$  for use in the more



exact computation of  $e$ . All this was carefully explained in all my early papers.<sup>7</sup> It is true that in my later papers,<sup>8</sup> after the existence of the electron had been demonstrated and its value accurately determined, I found it in the interests of both convenience and accuracy to use the value of  $e$  for working back to  $a$ , and this I often did, but it was in no way essential to my method and was actually never used until the value of  $e$  had been accurately found without it. *In other words, my method of determining the size of the carrier of the electric charge is in fact completely independent of every assumption about the value of this charge.*

3. It is fundamentally erroneous to suppose that the method used by several observers, including Sexl, of determining the radius of the drop by assuming its sphericity and density and then measuring its speed of fall at two different pressures is in any important respect an *essential* modification of my method, for *there is no relationship here involved that is not included in my linear relationship between  $e_1^{2/3}$  and  $l/a$ , or  $1/pa$ .* I exhibited my results in this single-line form because it is by far the most comprehensive and by far the most elegant mode of treatment of oil-drop data. It is simply Stokes' law, with a first correction term added, that requires the linear relation between  $v_1$  and  $l$ , mentioned by Sexl, and it is the same law plus the unitary character of electricity out of which grows the linear relation between  $e_1^{2/3}$  and  $l/a$ . The straight line between  $v$  and  $l$  is a different one for each drop because the drop-radius has not yet been eliminated from it. By its elimination in the  $e_1^{2/3}$ ,  $l/a$  line all of these  $v$ ,  $l$  lines have been reduced to a single one, as is beautifully shown in my published data.

Again, after I had changed both pressure ( $l$ ) and drop-radius  $a$  and found that 99 percent of my drops fell upon the single  $e^{2/3}$ ,  $l/a$  line it obviously became superfluous to change  $l$  alone as these other observers do, for if a point cannot get off the line by varying at random both  $l$  and  $a$  it clearly cannot do so by varying  $l$  alone and holding  $a$  constant.

Further, the reason that in my early experiments I did not change  $l$  alone in this way—an operation which takes a relatively long interval of time—was that on account of the slow change in size of all drops, especially of mercury drops, this method was less accurate than the one I did use of changing both  $l$  and  $a$  and thus getting a group of velocity-measurements close together in time and hence practically free from evaporation errors. If an occasional one of my points fell entirely off this line it meant, as I pointed out fifteen years ago, simply that this

<sup>7</sup> Millikan, Phys. Rev. (1) 32, 379 (1911)

<sup>8</sup> Millikan, Phil. Mag. 34, 3 (1917)

drop had not the assumed density or sphericity. It might, indeed, conceivably have meant, had the observation stood by itself, that the charge carried was a fraction of an electron while the assumed density and sphericity were correct. This was the way Ehrenhaft chose to interpret his irregularities, *but this alternative was barred out by the observed multiple relationship in speeds* and also by the fact that  $N_e$  when computed from Brownian movements came out as in electrolysis.<sup>9</sup> It became possible at once in the case of a drop that fell off my line, to obtain the correct equivalent density of a spherical drop by inserting such a density-value as would make the drop fall on that line. This is precisely what I did as early as 1911, and it is essentially what these other more recent observers, including Sexl, do when they work back to density or drop-radius from their  $v, l$  line, except that they ignore evaporation and in the case of mercury at least introduce large errors thereby.

It is true that Meyer and Gerlach<sup>10</sup> and Bär<sup>11</sup> performed an important service by computing the densities of particles produced by Ehrenhaft's method from the linear  $v, l$  relation instead of the linear  $e_1^{2/3}, l/a$  relation, such as I used, for though the two methods, in view of my multiple relationships, must yield the same results, barring evaporation, Meyer and Bär's result is, as they point out, entirely independent of the existence upon their particles of any charge at all, so that when they find by their procedure, as I had done from mine, that Ehrenhaft's assumed densities are entirely wrong they remove from him the possibility of calling upon any electrical assumption whatever, for explaining his irregularities. In other words, Meyer and Bär added a third demonstration, independent of the two that I used as mentioned above, that Ehrenhaft's irregularities are due to the assumption of incorrect drop densities. It may be added, too, that there is no apriori reason why some of Hake and Wasser's droplets may not be made up of clusters of particles of little more than molecular dimensions even though they are formed from the condensation of pure mercury, and such clusters may conceivably have a different long wave-length limit from that of mercury in mass. For it will be remembered that it requires light of wave-length about 1200 angstroms to detach electrons from mercury molecules, while the long wave-length limit of liquid mercury is 2635 angstroms. This point, however, will be settled by experiments now in progress.

In Derieux's work upon mercury, it was found impossible—as he clearly stated—to prevent evaporation, but by taking a series of consecutive

<sup>9</sup> Millikan, Phys. Rev. **8**, pp. 610-11 (1916).

<sup>10</sup> Meyer and Gerlach, Ann. d. Phys., **47**, 227, 1915.

<sup>11</sup> Bär, Ann. der Phys. **59**, 393 (1919) and Ann. der Phys. **67**, 157 (1922).

observations in rapid succession he was able to render its influence small and he then found, by assuming his drops spherical and of density 13.56, that all of his points fell close to a straight line of slope  $A = .708$  and having an intercept at the correct value for the electron. It then follows, as a matter of necessity, that if there had been no evaporation, and if the points had all been exactly on the .708 line, Sexl could not get by using Bär's method of computing drop-radius and density as he does (working back from the observed  $v, l$  line) different values of  $a$  and  $\sigma$  from those used by Derieux, unless one or the other of them made numerical blunders. It is not important to search for such blunders since Sexl's critique of Derieux's results is completely without significance because of his astonishing disregard of evaporation in spite of Derieux's full discussion of it.

NORMAN BRIDGE LABORATORY OF PHYSICS,  
CALIFORNIA INSTITUTE OF TECHNOLOGY,  
February 24, 1925.

ON ELSTER AND GEITEL'S THEORY OF THE  
ELECTRIFICATION OF RAIN DROPS

BY T. E. W. SCHUMANN

## ABSTRACT

Electrification of large drops by collision with small drops in an electric field.—The following experiments were made to test *Elster and Geitel's theory of the electrification of rain drops*. Large drops (A drops) falling between the horizontal parallel plates of a charged condenser, were sprayed from below with a fine stream of small drops (B drops) and the charge on the A drops was found to be of the same sign as that of the upper plate and to be proportional to the field strength. From the charge per A drop and the probable number of collisions with B drops, the charge per collision was computed and found to be zero for B drops of radius less than 0.18 mm and then to increase rapidly with the radius to 0.4 mm. Photographs taken with a motion picture camera show that the B drop first coalesces with the A drop and then, if its momentum is sufficient, a protuberance is produced on the upper surface of the A drop, which breaks up into a number of small droplets which carry off with them not only part of the A drop but also some charge. Very small B drops probably merely coalesce with A drops. In the case of falling rain, cloud droplets are too small to have a charging effect, and the effect of larger drops overtaking smaller ones is to weaken the existing field. Hence it is doubtful whether this phenomenon alone can explain the observed charges on raindrops and it certainly does not explain such high potential differences as occur in lightning discharges.

ELSTER and Geitel<sup>1</sup> proposed two theories to explain the electrical charge on rain, snow, etc. Geitel<sup>2</sup> gives a resumé of the second theory in the following way.

"Consider a falling drop of water in the normal electric field of the earth. The drop would be electrically polarized, the lower surface being positively charged, the upper surface taking on a negative charge. On its way to the earth it encounters a smaller drop whose terminal velocity is therefore less. When the smaller recoils from the lower surface of the larger, it takes along some positive charge, which is carried up along with it by the ascending air-currents. It is clear that the collision of the drops in this way would cause a *strengthening* of the existing field, the free charges (positive and negative) being carried against the lines of force. . . . And so there is a possibility that the existing field may be increased to such an extent that discharges (in the form of lightning) may at last take place."

<sup>1</sup> Elster and Geitel, *Phys. Zeits.* 14, 1287 (1913).

<sup>2</sup> H. Geitel, *Phys. Zeits.* 17, 455 (1916).

For the sake of brevity we shall in future refer to the large drops as A drops, and to the small ones as B drops.

In the older theory of Elster and Geitel, afterwards discarded by them, it was assumed that the B drops moved in the streamlines around an A drop, the last point of contact between the drops being on the upper surface of the A drop. In this case the electrical action is directly the opposite of that described above, i.e., the tendency is to weaken the existing field. The object of this work was to test these two theories experimentally.

#### DESCRIPTION OF THE APPARATUS

Large drops of water (A drops) are allowed to fall into a small vessel which is connected to a quadrant electrometer so that the charge on an A drop may be accurately measured. These drops fall through two holes cut centrally in the plates of a parallel-plate condenser mounted so that the gradient of the field is vertical.

A fine stream of B drops issues from a small orifice and is shot from below through two narrow slits cut in the condenser plates, so that it meets the falling A drops halfway between the plates, i.e. in an electric field of known and variable intensity. The customary insulating and shielding precautions are taken so that both the A and the B drops are initially uncharged. That this is the case can be further verified by measuring a charge on the A drops in a zero field. This was done and no charge was found.

#### EXPERIMENTAL RESULTS

As soon as an electric field was established the A drops showed a charge, caused by coming in contact with the B drops. The strength of the field was varied, and it was found that the charge was directly proportional to the field-strength when measured for a great number of drops, since the charge on a single drop is subject to probability fluctuations. The sign of the charge is in the sense of Elster and Geitel's first theory—in a normal field (top plate positive) the A drops are positively charged. It was therefore assumed that the B drops in some way travel around a falling A drop, and that contact is last made on the upper surface of the A drop.

The next step was to make quantitative measurements of the magnitude of the charge for a single collision. To do this the following determinations have to be made.

(a) The charge on an A drop could easily be determined, as remarked above, by measuring the charge on a counted number of A drops by

means of the quadrant electrometer, whose constants are readily measurable.

(b) The other quantity to be determined is  $n$ , the average number of B drops colliding with the A drop in any particular experiment. To determine  $n$  we measure the respective sizes of the A and B drops, their respective velocities at the point of collision, and the weight of B drops passing per second. Knowing these the calculation of  $n$  is a mathematical problem,<sup>3</sup> and the average charge  $e$  produced by a single encounter is got by dividing the charge of the A drop by  $n$ .

To fix our ideas and to get a measure of the extent to which charging takes place, we introduce the following considerations. The maximum charge which a small sphere can obtain by contact with a large electrically neutral sphere which is polarized by a uniform electric field of intensity  $F$ , is given by the expression<sup>4</sup>  $\frac{1}{2}\pi^2 \cdot Fr^2$  where  $r$  is the radius of the small sphere. Although this represents a highly idealized case, and would not at all apply rigidly to our A and B drops, which naturally change their shape, and even coalesce, as we shall see later on, yet we can use this expression quite conveniently to define the extent to which charging takes place. Let

$$k = 2e/n\pi^2 Fr^2$$

Then  $k$  is the ratio of the experimental charge on a B drop to this maximum theoretical charge, and is a measure of the electrical action.

It was found that the value of  $k$  depends mainly on the size of the B drops, a variation in the size of the A drops making very little difference, provided they remained fairly large compared with the B drops. The relative velocities employed were of the order of the difference between the terminal velocities of the A and B drops when falling freely in air at atmospheric pressure. Small variations in this relative velocity did not seem to affect the value of  $k$  to any appreciable extent. However, it is probable that the relative velocity plays a very important part: for a certain size of B drop a small variation in the relative velocity may very likely cause quite a large variation in  $k$ . This point, however, was not carefully investigated, because at the time when these experiments were performed the mechanism of collision, as revealed by photographs taken at a much later date, was not fully understood. A table follows giving the value of  $k$  for different sizes of B drops.

Radius of B drops	$k$
0.363 mm	0.77
0.250	0.61
0.185	0.075
0.179	0.013
0.148	-0.002

<sup>3</sup> For complete details see T. Schumann, Göttingen Dissertation 1924.

<sup>4</sup> Poisson, Mem. de l'Inst. (1811) p. 196.

To explain the values thus obtained it was at first assumed that in some way or other the B drops go *around* the A drops, the last point of contact between two drops being on the upper surface of the A drop. The larger the B drop the further it goes around, and the last point of contact is therefore in a region where the surface density on the A drop has a high value. When the radius of the B drop  $r$  is reduced to about 0.18 mm it goes no further than the horizontal equator of the A drop. Here the surface density is zero and hence the B drop remains uncharged. As it was found impossible to produce uncharged B drops of a size smaller than 0.15 mm radius it was attempted to extend the table on theoretical grounds.<sup>5</sup> Making certain simplifying assumptions concerning the elastic impact between the drops, and taking into account the tendency of very small B drops to be carried in the streamlines of the air around a falling A drop, it was calculated that  $k$  would reach a *minimum* value of about  $-0.4$  when  $r$  has the value of 0.03 mm, and tends towards zero when  $r$  becomes zero. A negative value of  $k$  means that the effect is reversed, i.e., the action would be in accord with Elster and Geitel's second theory, where it was supposed that the tendency is to strengthen the existing field. The above work was carried out at Göttingen, Germany.

It was felt, however, that the supposed motion of the B drops *around* the A drops was rather remarkable. Furthermore, the assumption that electrical contact between two drops is possible without their coalescing, hardly seems plausible. It was therefore decided to get photographic evidence of the manner in which drops of different sizes actually do behave when colliding. This part of the work was done at Yale University. As before, large drops fell through a stream of ascending B drops, and a rapid cinemetographic record was obtained of their motion.

Fig. 1 gives an example of many similar photographs obtained. Starting from the top right-hand corner and ending at the bottom left-hand corner, the downward motion of several large drops may be followed until after collision with the upward-moving small drops. As the photographs show, the drops first coalesce, but the momentum of the small drop carries it on, and produces a protuberance on the upper surface of the A drop, and this protuberance breaks up into a number of small drops. A small part of the large drop is thus actually *torn off* from its upper surface. This curious action completely explains the experimental results contained in the table given above. The small drops, breaking off at the top, carry along a negative charge with them (the field being normal), and the large drops convey a corresponding positive charge down to

<sup>5</sup> T. Schumann loc. cit.<sup>3</sup>



earth. Furthermore, it is highly probable that when the B drops are below a certain size, say 0.18 mm radius, their momentum would be too small to accomplish this tearing-off, and they would simply coalesce with the large drops. From this it is clear that the electrical action would not only depend upon the size of the B drops, but also on their relative velocity with respect to the A drops. Unfortunately in these experiments sufficient account was not taken of this fact. To approximate to the condi-

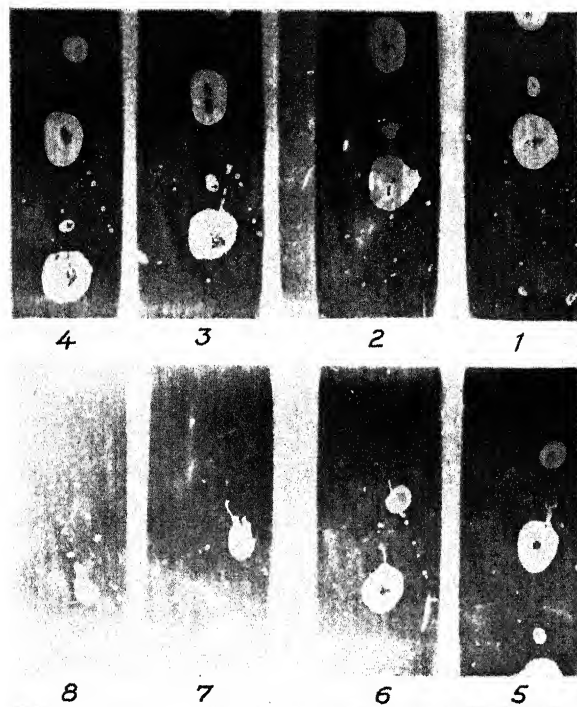


Fig. 1. Photos obtained with a motion picture camera, showing B drops passing through an A drop

tions in nature the relative velocity of a B drop with respect to an A drop should equal the difference of their terminal velocities falling in air of about atmospheric pressure.

#### CONCLUSION

Taking account of the experimental results obtained, we are inclined to believe that if the B drops have a radius below 0.18 mm they have no charging effect on larger drops, but probably coalesce with the large drops; or if they do rebound no electrical contact takes place and no

charging can result. The average radius of the drops that constitute the clouds is 0.01 mm so that as far as the action between cloud-drops and raindrops is concerned, Elster and Geitel's theory does not hold. If this is true, the theory loses its chief significance. For *raindrops* of different sizes, however, a modified form of their older theory does hold. Since this action has the tendency to weaken the existing field, their hypothesis about the production of potential differences between clouds and earth high enough to produce lightning must be discarded.

The only directly observable effect that we would expect, according to the results obtained, would be a weakening of the earth's field at the moment that the first raindrops begin to fall. The largest raindrops, having the greatest terminal velocity, would naturally reach the earth's surface first (unless they have to travel much further than the smaller drops), and if on their way they have come in contact with smaller raindrops, the charge would be such as to decrease the potential gradient. To get a more complete knowledge of the actual phenomena in nature it would be necessary to take simultaneous observations of the charges on rain and of the alterations in the potential gradient of the earth's electric field.

The author wishes to express his thanks to Prof. E. Wiechert, Director of the Geophysical Institute at Göttingen, who suggested this research, and to Prof. J. Zeleny of Yale, for his helpful interest in the latter part of the work.

DEPARTMENT OF PHYSICS,  
YALE UNIVERSITY,  
December 23, 1924.

## ON THE QUANTITATIVE THEORY OF ELECTROSTATIC SYSTEMS

BY A. W. SIMON

## ABSTRACT

General theory of cyclic electrostatic machines.—It is shown that if any system of insulated conductors is carried through a periodic cycle of electrostatic operations, the potential of any conductor of the system after  $n$  such cycles can be expressed in the form of a recurrent sequence. A general formula is then deduced for the potential of any conductor of the system after  $n$  cycles. The application of the formula to the case of electrostatic generators, electrostatic alternators, and electrostatic voltage multipliers is discussed. Methods of solution (1) for the case of a symmetrical alternator consisting of  $m$  inductors and  $m$  carriers so constructed that each carrier as it comes in front of an inductor is connected to the next following inductor, (2) for the Wimshurst alternator of four inductors and (3) for a new type of symmetrical alternator derived from the Wimshurst alternator by doubling the number of inductors. Finally it is shown how a simple electrostatic system can be made to function as a generator, alternator, or a voltage multiplier merely by a change of connections.

THE quantitative theory recently given for the influence electrostatic generator<sup>1</sup> can be immediately generalized to apply to any system of insulated conductors which are originally raised to various potentials and are then carried through a periodic cycle of electrostatic operations, if we define an electrostatic operation as (1) a moving about of the conductors of the system or (2) a making or breaking contact between any number of conductors of the system. If the system is under the action of only its own field, that is if none of the conductors are connected to sources of constant potential, then exactly the same reasoning given for the case of the influence electrostatic generator serves to establish the following general theorem:

If any electrostatic system is carried through a periodic cycle of electrostatic operations, the potential of any conductor of the system after  $n$  cycles satisfies an equation of the form

$$V_{n+m} + k_{m-1}V_{n+m-1} + k_{m-2}V_{n+m-2} + \cdots + k_0V_n = 0 \quad (1)$$

where the  $k$ 's are functions only of the electric coefficients of the elements in certain configurations of the cycle, namely those in which a change of charge occurs on any of the elements.

<sup>1</sup> A. W. Simon, Proc. Nat. Acad. 10, 302 (1924); Phys. Rev. 24, 690 (1924).

Now Eq. (1) expresses the potential of an element in the form of a recurrent sequence, which can be evaluated by methods of the calculus of finite differences.

The solution<sup>2</sup> of (1) depends on the nature of the roots of the corresponding algebraic equation

$$r^m + k_{m-1}r^{m-1} + k_{m-2}r^{m-2} + \dots + k_0 = 0 \quad (2)$$

If Eq. (2) has  $p$  pairs of imaginary roots of the form  $\alpha_i \pm i\beta_i$ , and consequently  $(m-2p)$  real roots, none of which are repeated, then the general solution of (1) takes the form

$$V_n = \sum_{j=1}^{j=m-2p} C_j r_j^n + \sum_{j=1}^{j=p} \rho_j^n (C_{1,j} \cos n\theta_j + C_{2,j} \sin n\theta_j) \quad (3)$$

where the  $C$ 's are arbitrary constants,  $r_j$  is a real root of (2), and  $\theta_j$  and  $\rho_j$  are given respectively by  $\tan \theta_j = \beta_j/\alpha_j$ ;  $\rho_j = \sqrt{\alpha_j^2 + \beta_j^2}$ . Eq. (3) is the fundamental equation of all purely influence static machines. These may be divided into two classes: (1) Electrostatic generators (predominant roots real) as exemplified by machines of the Voss or Toepler Holtz type,<sup>3</sup> and (2) electrostatic alternators (predominant roots imaginary) as exemplified by a machine recently described.<sup>4</sup>

If next we examine systems in which some of the conductors are connected to sources of constant potential while the system is carried through its cycle, we find that for this case the potential of any conductor satisfies an equation of the form

$$V_{n+m} + k_{m-1}V_{n+m-1} + k_{m-2}V_{n+m-2} + \dots + k_0V_n = K \quad (4)$$

where the small  $k$ 's satisfy the same conditions as before, while  $K$  is a function of both the electric coefficients of the elements in certain configurations and of the constant voltages impressed on the system. Now the solution of (4) is the sum of the general solution of (4) with the second member equal to zero, i.e. a solution of the form (3), and a particular solution of (4). This particular solution is

$$V_n = K/(1 + k_{m-1} + k_{m-2} + \dots + k_0) \quad (5)$$

as can readily be verified.

Eqs. (3) and (5) together are the fundamental equations of a class of static machines known as electrostatic voltage multipliers, which have recently been described in detail elsewhere.<sup>5</sup>

<sup>2</sup> G. Boole, *A Treatise on the Calculus of Finite Differences*, Chap. XI.

<sup>3</sup> A. W. Simon, *Phil. Mag.* **49**, 257 (1925).

<sup>4</sup> A. W. Simon, *Phys. Rev.* **25**, 268 (March 1925).

<sup>5</sup> A. W. Simon, *J. Opt. Soc.* **9**, 345 (1924); also **10**, 669 (June 1925).

The solution of (1), as has been pointed out, depends on the possibility of finding the roots of Eq. (2), and while this cannot be done in every case, there are a number of special cases where this can be done readily, and these we shall now consider.

### 1. SYMMETRICAL ELECTROSTATIC ALTERNATORS

These machines consist of  $m$  inductors and  $m$  carriers symmetrically mounted, and are so constructed that each carrier as it comes in front of an inductor is connected to the  $i$ th inductor following in the direction of rotation. The particular machine corresponding to  $m=5$  and  $i=1$ , is shown in Fig. 1. If we set up the equations for such a machine, ( $i=1$ ), we find that the potentials of the  $n$ th and  $(n+1)$ st cycles are related by a system of equations of which the left members take the form:

$$\begin{array}{l} aV_{1,n+1} + eV_{3,n+1} + dV_{5,n+1} + cV_{7,n+1} + bV_{9,n+1} \\ b \text{ " } + a \text{ " } + e \text{ " } + d \text{ " } + c \text{ " } \\ c \text{ " } + b \text{ " } + a \text{ " } + e \text{ " } + d \text{ " } \\ d \text{ " } + c \text{ " } + b \text{ " } + a \text{ " } + e \text{ " } \\ e \text{ " } + d \text{ " } + c \text{ " } + b \text{ " } + a \text{ " } \end{array}$$

and the right members, similarly:

$$\begin{array}{l} a'V_{1,n} + e'V_{3,n} + d'V_{5,n} + c'V_{7,n} + b'V_{9,n} \\ b' \text{ " } + a' \text{ " } + e' \text{ " } + d' \text{ " } + c' \text{ " } \\ c' \text{ " } + b' \text{ " } + a' \text{ " } + e' \text{ " } + d' \text{ " } \\ d' \text{ " } + c' \text{ " } + b' \text{ " } + a' \text{ " } + e' \text{ " } \\ e' \text{ " } + d' \text{ " } + c' \text{ " } + b' \text{ " } + a' \text{ " } \end{array}$$

By the introduction of the symbolic operator  $r$ , which we define to be the same as the symbolic operator  $E$  of the calculus of finite differences,<sup>6</sup> we can write the above set of equations in the form

$$\begin{aligned} (ar - a')V_{1,n} + (er - e')V_{3,n} + (dr - d')V_{5,n} + (cr - c')V_{7,n} + (br - b')V_{9,n} &= 0 \\ (br - b') \text{ " } + (ar - a') \text{ " } + (er - e') \text{ " } + (dr - d') \text{ " } + (cr - c') \text{ " } &= 0 \\ (cr - c') \text{ " } + (br - b') \text{ " } + (ar - a') \text{ " } + (er - e') \text{ " } + (dr - d') \text{ " } &= 0 \quad (8) \\ (dr - d') \text{ " } + (cr - c') \text{ " } + (br - b') \text{ " } + (ar - a') \text{ " } + (er - e') \text{ " } &= 0 \\ (er - e') \text{ " } + (dr - d') \text{ " } + (cr - c') \text{ " } + (br - b') \text{ " } + (ar - a') \text{ " } &= 0 \end{aligned}$$

If we solve for each of the unknowns in turn, we have

<sup>6</sup> Boole, loc. cit.<sup>2</sup> p. 16.

$f(r)V_{1,n}=0, f(r)V_{3,n}=0, f(r)V_{5,n}=0, f(r)V_{7,n}=0, f(r)V_{9,n}=0, \quad (9)$   
 where  $f(r)$  is given by

$$f(r) = \begin{vmatrix} (ar-a') & (er-e') & (dr-d') & (cr-c') & (br-b') \\ (br-b') & (ar-a') & (er-e') & (dr-d') & (cr-c') \\ (cr-c') & (br-b') & (ar-a') & (er-e') & (dr-d') \\ (dr-d') & (cr-c') & (br-b') & (ar-a') & (er-e') \\ (er-e') & (dr-d') & (cr-c') & (br-b') & (ar-a') \end{vmatrix}$$

Since  $f(r)$  is the same for all of the potentials, it follows that the roots which enter into Eq. (3) for this system are the same; and this is found to be true for every purely influence system. The arbitrary constants, however, are different for each potential.

Attention may be directed to the form of this determinant, namely that it is a cyclic determinant or circulant. For the five inductor alternator it is of the fifth order; for an  $m$  inductor alternator it would be a cyclic determinant of the  $m$ th order.

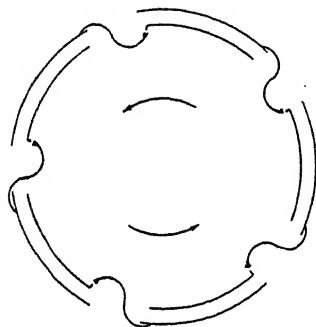


Fig. 1. A five inductor electrostatic alternator.

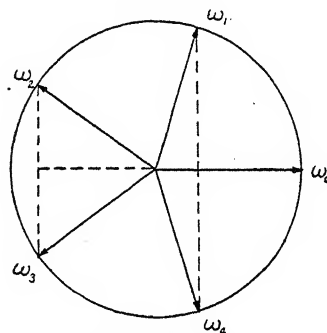


Fig. 2. The five fifth roots of unity, which play an important part in the theory of the alternator of Fig. 1.

Now a cyclic determinant of order  $m$  has the important property that it can be broken up into  $m$  factors which are rational functions of the elements of the determinant and the  $m$ th roots of unity.<sup>7</sup> Each of these factors is linear in  $r$ , and by equating each separately to zero, we obtain the  $m$  roots desired.

The close connection between the geometry of these machines and the geometry of the roots of unity is extremely interesting. (Compare Figs. 1 and 2, which illustrate the case for  $m=5$ .)

<sup>7</sup> Pascal (Leitzmann), *Die Determinanten*, p. 73.

2. THE WIMSHURST ALTERNATOR<sup>8</sup>

This machine (Fig. 3) gives rise to a determinant of the form

$$f(r) = \begin{vmatrix} M_1 & M_2 \\ M_3 & M_4 \end{vmatrix}$$

where each of the matrices  $M_i$  is a cyclic matrix of the fourth order. By subtracting the third row (in each matrix) from the first, and the fourth row from the second, and then adding the third column to the first, and the fourth to the second, the determinant splits up into the product of two other determinants of the form

$$\begin{vmatrix} a & b & c & d \\ b & a & d & c \\ e & f & g & h \\ f & e & h & g \end{vmatrix} \begin{vmatrix} a-b & c-d \\ b & a & d & c \\ e-f & g-h \\ f & e & h & g \end{vmatrix}$$

and these in turn can be broken up into four factors, namely:

$$\begin{vmatrix} b+a & d+c \\ f+e & h+g \end{vmatrix} \begin{vmatrix} b-a & d-c \\ f-e & h-g \end{vmatrix} \begin{vmatrix} a+bi & c+di \\ e+fi & g+hi \end{vmatrix} \begin{vmatrix} a-bi & c-di \\ e-fi & g-hi \end{vmatrix}$$

Each of these factors is quadratic in  $r$ , and by equating each of the four separately to zero and solving for  $r$ , we obtain the eight roots required.

Unfortunately, if the number of inductors exceeds four, this process fails. This suggests that in a certain sense the Wimshurst alternator is not perfectly symmetrical, and, in fact, if we add 4 additional inductors placed as in Fig. 4, we convert the Wimshurst alternator into a new one which is perfectly symmetrical and again leads to a cyclic determinant. Moreover, we can immediately extend the theory to machines of this type with more than four inductors.

Let us now turn to a consideration of the roots themselves. At the outset we may divide these (both real and imaginary) into three classes according as their ab-

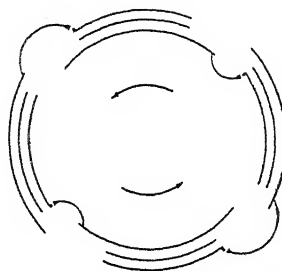


Fig. 3. The Wimshurst alternator of 1891.

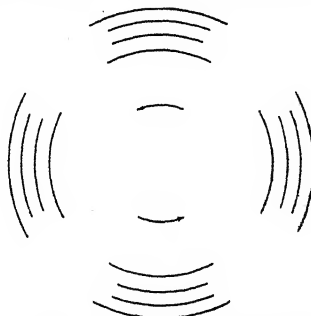


Fig. 4. A perfectly symmetrical electrostatic alternator. Any carrier (smaller arcs) is connected to the inductor (larger arcs) next following in the direction of rotation and situated on the opposite side. The inductors are fixed, the carriers rotate.

<sup>8</sup> J. Wimshurst, Phil. Mag. 31, 507 (1891).



solute value is (1) less than unity, (2) equal to unity, or (3) greater than unity. In the first case the corresponding terms are transient terms, which vanish for large values of  $n$ ; in the second, the corresponding terms are constants; and in the third they are permanent terms, which approach infinity as  $n$  approaches infinity.

Since the  $k$ 's are functions only of the electric coefficients, the roots also will be functions only of the electric coefficients; and further it turns out that they are always ratios, or pure numbers.

In many cases it is possible to determine, from the known properties of electric coefficients, what range of values in general the roots may take, irrespective of what the particular values of the coefficients may be. For example in the case of a symmetrical Kelvin replenisher<sup>9</sup> of two carriers, it is possible to show that one of the roots is always less in absolute value than unity, irrespective of what the relative dimensions of inductors and carriers, angle at which the polarizing rod is set, etc.

In the case of the electrostatic alternators which lead to cyclic determinants, we obtain the roots in the form:

$$r = (A_1 + B_1 i) / (A_2 + B_2 i)$$

whence

$$\rho = \sqrt{(A_1^2 + B_1^2) / (A_2^2 + B_2^2)}$$

and

$$\tan \theta = (A_2 B_1 - A_1 B_2) / (A_1 A_2 + B_1 B_2)$$

If we put  $B_1/A_1 = \tan \theta_1$  and  $B_2/A_2 = \tan \theta_2$  we have further

$$\tan \theta = \tan (\theta_1 - \theta_2).$$

The latter formula is a very convenient one for the calculation of the period of the alternator; in many cases it is found that  $\theta_2 = 0$  whence

$$\tan \theta = \tan \theta_1.$$

The range of values which  $\theta$  and  $\rho$  may take can also be established in many cases, and it is important to note that  $\theta$  and  $\rho$  are functions of the electric coefficients of the elements of the machine, so that the period of reversal, which is determined by the magnitude of  $\theta$ , can be varied by varying the relative capacities (electric coefficients) of the elements of the machine. The values of the  $\rho$ 's will determine whether or not the machine is self-exciting; if one of the  $\rho$ 's is greater than unity, the machine is self-exciting, and the greater the values of the  $\rho$ 's the more rapidly the machine builds up.

We have now indicated in a general way how the quantitative theory of electrostatic systems may be developed, and have briefly indicated the

<sup>9</sup> A. W. Simon, loc. cit.<sup>1</sup>

properties of these systems. We have noted that these systems are of three general types, (1) alternating systems, as exemplified by electrostatic alternators; (2) generating systems, as exemplified by machines of the Toepler-Holtz or Voss type; and (3) constant potential systems, as exemplified by electrostatic voltage multipliers.

As our final point we shall draw attention to a simple electrostatic system which can be converted at will to any one of these three types by merely changing the connections. The system, which consists of four

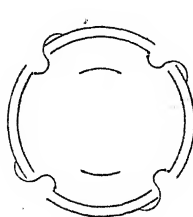


Fig. 5. An electrostatic system connected as an alternator.

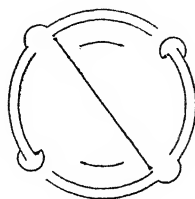


Fig. 6. The system of Fig. 5 connected as a generator.

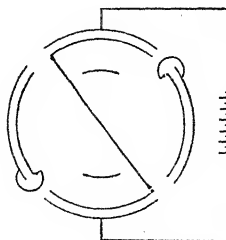


Fig. 7. The system of Fig. 5 connected as an electrostatic voltage multiplier.

fixed inductors and four revolving carriers, when connected as in Fig. 5 is an alternator; when connected as in Fig. 6 an ordinary static machine of the Voss type; and finally when connected as in Fig. 7, a constant potential machine.

In conclusion I wish to thank Prof. A. H. Compton for the encouragement he has given me in this work, as well as Mr. R. W. Barnard of the Mathematics Department for many helpful suggestions he has made regarding the mathematical treatment of the problem.

RYERSON LABORATORY,  
UNIVERSITY OF CHICAGO,  
March 25, 1925.

POTENTIOMETER ARRANGEMENT FOR MEASURING  
MICROVOLTAGES AT RADIO FREQUENCIES

BY AXEL G. JENSEN

## ABSTRACT

The arrangement described enables voltages down to about 0.1 microvolt to be measured to within about one percent. The resistance units are wound non-inductively on a toroid so as to reduce the lengths of connecting wires to a minimum. Up to frequencies of  $3 \times 10^6$  cycles, the impedance of such a unit is less than one per cent higher than the pure resistance. The potentiometer is built compactly to minimize capacity effects and for convenient use in the field.

IN the February number of the Review there appears an article by A. W. Hull and W. H. Williams<sup>1</sup> in which the authors describe a method for measuring microvoltages at radio frequencies. It is stated in this article that voltages of the order of 5-150 microvolts have never been accurately measured before at these frequencies and also that the use of a resistance potentiometer is out of the question for these small voltages on account of the inductive drop in the wire.

It may be of interest to your readers to know then, that the American Telephone and Telegraph Company and the Bell Telephone Laboratories, Incorporated, have for some time past been measuring voltages of this order of magnitude in connection with their measurements of field strengths from broadcasting stations, and furthermore, in measuring these voltages, are using a resistance potentiometer arrangement, which allows measurements of voltages down to about  $1/5$  of a microvolt with an accuracy of about one percent.

In the accompanying figure there is shown a schematic diagram of the potentiometer arrangement in connection with a receiving set for radio signals.

The current  $I$  from the vacuum tube generator flows through a 700-ohm thermocouple in connection with a Weston micro-ammeter, and from the thermocouple passes through the potentiometer  $P$ .

The resistance units in this potentiometer are wound non-inductively (reverse loop winding) on a hard-rubber toroid so that the points  $a$  and  $e$  are close together and the points  $e$  and  $c$  directly opposite on the toroid, thereby reducing the length of the connecting wires  $abe$  and  $cde$  to a minimum.

<sup>1</sup> Hull and Williams, Phys. Rev. 25, 147 (February 1925).

The capacity of such a non-inductive winding is small and the inductance may be calculated by the following formula<sup>2</sup>

$$L = 2l(\log_e d/\rho + 1/4 - A)$$

in which  $l$  is the total length of wire,  $\rho$  the radius of wire,  $d$  the distance between adjacent turns, and  $A$  a constant varying from 0 to .45 as the number of turns varies from 0 to infinity. The value of  $A$  is .25 for a coil of four turns, and it will therefore be safe to disregard the two last terms in the formula, since all the coils in the potentiometer have more than four turns. Applying this formula to the coarsest wire used in the potentiometer, namely No. 36 B. & S. manganin wire D.S.C., we get  $d/\rho = 3.5$  and thus  $L = 2.45$  cm per unit length, while the resistance of the wire is 30 ohms per unit length.

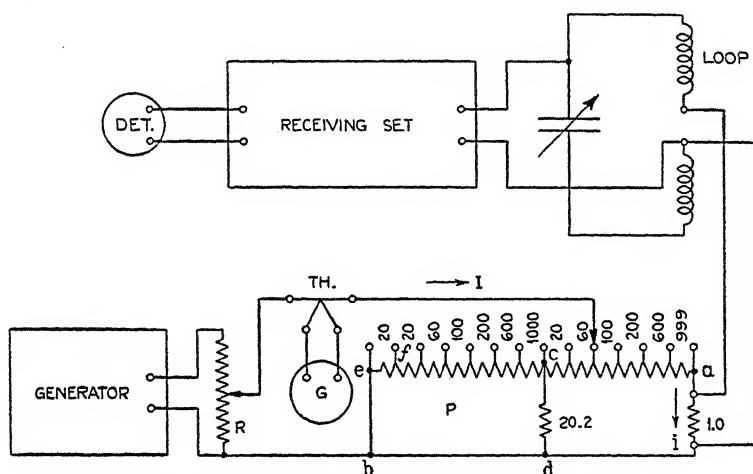


Fig. 1. Diagram of potentiometer arrangement.

This gives at 750,000 cycles an inductive drop which is 3.5 percent of the resistance drop and thus an impedance which is equal to  $\sqrt{1^2 + .035^2}$  or 1.0006 times the pure resistance of the wire. It will be seen that not until the frequency is increased to about 3,000,000 cycles will the impedance be as much as one percent higher than the pure resistance.

For the finer wire the relative excess of inductive drop over resistance drop will be still smaller, so that the entire potentiometer will attenuate the current with an accuracy of one percent or better up to frequencies of about 3,000,000 cycles.

The one ohm unit in the output side of the potentiometer is made up of a piece of No. 36 manganin wire approximately 3.5 cm in length and

<sup>2</sup> See E. B. Rosa, Bull. Bur. Stand. 4, 301 (1907-8).

arranged bifilar so that we may use the same formula as before in calculating the inductance. We have here  $A=0$  and  $d/\rho$  approximately 5, so that  $L=13$  cm and  $\omega L=.06$  ohm at 750,000 cycles. The impedance is thus approximately 1.002 ohm or only 1/5 percent higher than the pure resistance.

The highest current attenuation is obtained with the movable arm of the potentiometer at  $f$ , in which case the output current  $i$  is 10,000 times smaller than the input current  $I$ , and since the thermocouple combination used will measure one milli-ampere conveniently it is possible to determine voltages down to about 1/10 microvolt with an accuracy of one percent or better.

By means of the potentiometer shown in the figure the following ratios of  $i/I$  can be obtained: .0001; .0002; .0005; .001; .002; .005; .01; .02; .05; .1; .2; .5 and 1.0. These ratios were checked step by step at 750,000 cycles by means of a calibrated detector meter in the output of the highly sensitive receiving set connected up to the potentiometer, and in no case was the discrepancy between the calculated value and the measured value found to be more than one percent.

The potentiometer is built very compactly in order to minimize capacity effects; in fact, the entire potentiometer including the switch is enclosed in a copper can 3 inches in diameter and 3 inches high. The potentiometer, thermocouple, meter, and current adjusting rheostats are all contained in a copper box  $10 \times 7 \times 7$  inches, and the generator is enclosed in a similar box so that the complete measuring equipment may be used conveniently in the field in connection with a portable receiving set.

In cases where portability is not essential it should be possible to measure still smaller voltages by using a sensitive galvanometer in connection with the thermocouple. Also it should be possible to increase the sensitivity of the arrangement still further by replacing the one ohm output resistance by a small known inductance, for instance of the type described by Hull and Williams.

BELL TELEPHONE LABORATORIES, INCORPORATED,  
RESEARCH DEPARTMENT,  
NEW YORK, N. Y.  
March 13, 1925.

VARIATION OF YOUNG'S MODULUS WITH TEMPERATURE  
FROM VIBRATION MEASUREMENTS

A. L. KIMBALL, JR. AND D. E. LOVELL

## ABSTRACT

A tuning fork of the metal being studied was mounted in an electric furnace and one prong was connected by means of a thread to a stylus which recorded the motion of the prong on a moving plate. Thus the frequency was measured to 1/10 percent. Curves obtained for a 3.5 percent nickel steel and for a soft machine steel (.15 percent C) are practically identical, the modulus decreasing 10 percent as the temperature increased from 20° to 350°C and 16.7 percent for the change from 20° to 500°C. This suggests that the temperature variations of the modulus may be a fundamental property of the atoms, unaffected by the size of the crystals.

## PURPOSE AND SCOPE OF INVESTIGATION

ALTHOUGH previous work has been done in this field, the results obtained, even for a substance of the same composition, have shown wide variations with different investigators. Furthermore, owing to the tendency of a metal, such as steel, to assume a very slight plastic deformation under stress, which increases with time, the usual statical method of point by point deflections is subject to error. The length of time which is required in making the observations may have a decided effect in accurate work.

In order to overcome this difficulty, in this work the variation of Young's modulus with temperature was determined from accurate measurements of the frequencies of tuning forks, a method which appears to have been little used.<sup>1</sup> The amplitude of the vibrations was comparatively small, so that the maximum stress was less than one tenth of the elastic limit of the material. The frequency was about 20 cycles per second, so that each stress cycle during the vibration required about 1/20 of a second for its performance.

## APPARATUS AND METHOD

The apparatus is shown in Fig. 1. The fork *F*, with prongs about 55 cm long by 2.5 cm wide by .64 cm thick, was clamped in the asbestos oven heated by an electric coil. The clip *A* was suddenly pulled off the

<sup>1</sup> K. R. Koch and R. Dieterle, *Ann. der Phys.* **68**, 441 (1922);  
Mallock, *Proc. Roy. Soc.* **A95**, 429 (1919);  
H. M. Dadourien, *Phys. Rev.* **13**, 337 (1919);  
Iokibe and Sakai, *Phil. Mag.* **42**, 397 (1921).

tips of the fork, starting a vibration about one quarter of an inch in amplitude. One side of the fork was connected to a fine wire *W* which passed through a small hole in the oven and was attached to a light wooden stylus *S* with a needle point on its end. The wire was kept taut by a small spring so that the tip of the stylus followed the vibratory motion of the fork exactly. Time was recorded by another stylus which registered seconds from a seconds pendulum. The vibration and time records were traced side by side on the smoked glass plate about one meter long which was pulled along at a constant rate of about 4 cm per second by an electric motor. With this apparatus it was possible to obtain frequency measurements accurate to within less than 1/10 percent. This required that the temperature be measured to within a degree or two, in order that errors from this cause be kept within the same limit.

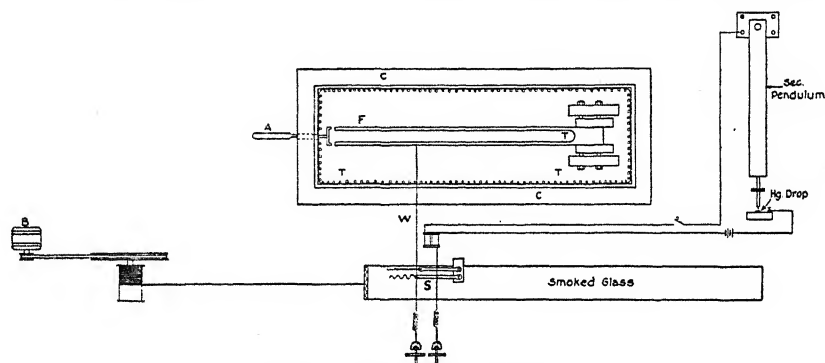


Fig. 1. Diagram of apparatus.

A uniform temperature distribution in the fork was produced by placing over it a conducting shield of sheet copper not shown in the figure. Temperatures up to 350°C were measured by mercury thermometers, and for higher temperatures a thermocouple was used. By trials and suitable calibrations, it was found that an accuracy of within one or two degrees could be obtained.

### RESULTS

Two different kinds of steel were tested in this study, 3.5 percent nickel steel and 0.15 percent commercial carbon steel.

A complete series of observations was taken upon two 3.5 percent nickel steel forks of the form shown in Fig. 1, each machined out of a single piece of heat treated steel. A series of measurements also was made upon a pair of 3.5 percent nickel steel bars clamped together in the form of a fork. All of the nickel steel was of the same chemical composition which



was as follows: C, .35 percent; Si, .21 percent; S, .020 percent; P, .018 percent; Mn, .58 percent; Ni, 3.52 percent.

The heat treatment consisted of oil quenching at 850°C and drawing at 650°C. The size of the bars from which the test pieces were cut was 100×9×4.2 cm. The plane in which vibrations took place was perpendicular to the plane of rolling of these bars.

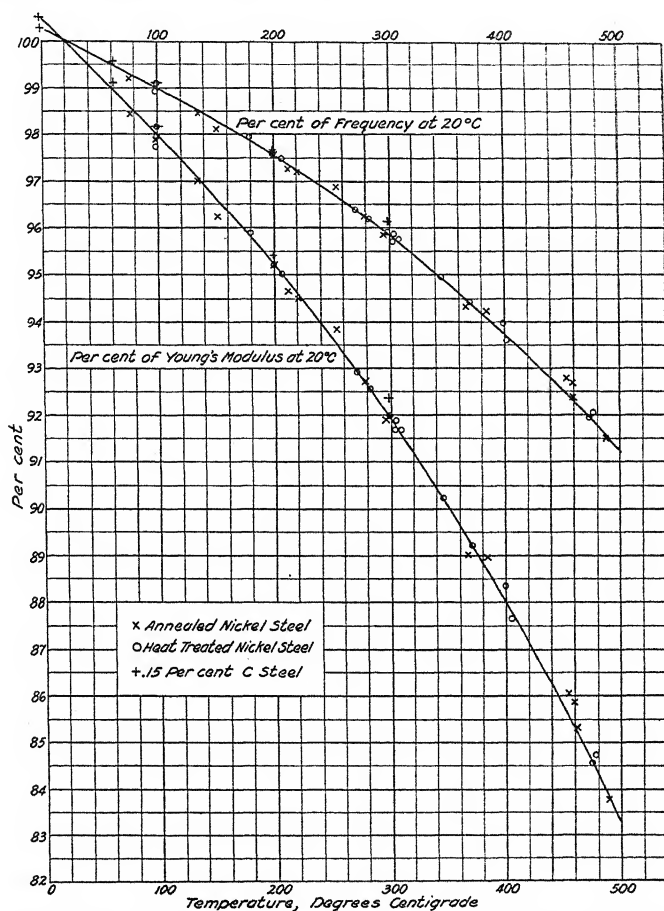


Fig. 2. Curves showing decrease of Young's modulus with temperature for 3.5 percent nickel steel and .15 percent carbon steel.

The .15 percent carbon steel was an ordinary machine steel. The tests were made on a pair of bars clamped together in the form of a fork.

The curves in Fig. 2 show the final results of the measurements. The upper one shows the decrease in vibration frequency with increase of temperature and the lower one the corresponding decrease in Young's modulus, in each case measured in percent of the value for 20°C. The

curve for Young's modulus was obtained directly from the frequency curve by using the relation

$$f = K\sqrt{E/\rho}$$

where  $f$  = frequency

$E$  = Young's modulus

$\rho$  = density

$K$  = proportionality factor depending upon the shape of the vibrating body and its mode of vibration.

A small correction was necessary because the linear dimensions of the vibrating fork increase with temperature and the density  $\rho$  decreases.<sup>2</sup> Every point on the curves represents the average of from one to five records in each of which the frequency was determined from the average of from four to eight measurements.

A word should be said about the effect of various damping forces upon the frequency. It is well known that the period of a natural vibration is decreased slightly under the influence of damping. This effect was looked for in these experiments but was found to be within the limits of error. When a suitable friction was applied so as to increase the decrement four or five times, no change in frequency could be detected. Since the applied frictional force was much greater than that of the air, it was concluded that the effect of air friction on frequency was negligible. When the temperature was above 400°C the damping was notably greater, but even here the change in frequency, due to this cause, was within the limits of error.

The most interesting thing about the curves obtained seems to be that all points fall upon a continuous curve, or very nearly so, whether the nickel steel or the carbon steel was tested and whether the nickel steel was heat treated or annealed. This result suggests that the temperature variation of Young's modulus for these metals is little affected by variation of the size and arrangement of the crystals, but is a more fundamental property which is related to the atoms themselves.

These results are interesting in view of the fact that "elinvar," an alloy which shows practically no variation of Young's modulus with temperature, is also a nickel iron alloy. The nickel content of elinvar, however, is over 30 percent. The various peculiarities of nickel iron alloys of this type have been the subject of special investigations.<sup>3</sup>

RESEARCH LABORATORY,  
GENERAL ELECTRIC COMPANY,  
SCHENECTADY,  
December 31, 1924.

<sup>2</sup> Barton, Text Book of Sound, p. 298.

<sup>3</sup> G. E. Guillaume, Proc. Phys. Soc. London, 32, 374-404 (1920).

## AN APPROXIMATE DETERMINATION OF THE DEPTH OF COMPRESSION IN COPPER BARS DURING IMPACT

BY E. W. TSCHUDI

## ABSTRACT

Duration of impact of copper bars and of copper plated steel bars.—As in previous experiments, the duration of impact was measured by means of a Duddell-type oscillograph connected in series with the pair of colliding bars, each of which was suspended by four wires adjusted so that the plane ends struck squarely. In all cases the mass of each bar tested was the same, 2400 gm. By trying three diameters of contact area  $d$ , it was found that the time varies as  $1/d^{1/2}$ ; it also varies as  $1/v^{1/5}$ ; hence  $t = A/d^{1/2}v^{1/5}$ , where  $A$  has the values  $9.7 \times 10^{-4}$  and  $12.35 \times 10^{-4}$  c.g.s. units for these steel and copper bars. The steel bars were then plated with coherent copper deposited electrolytically to thicknesses of .017, .038, .064 mm. The time for the two thick films came out the same as for solid copper, while that for the thinnest film was between that for copper and that for steel. These results indicate that the thickness of the surface layer whose elastic constants determine the time of impact is only about .03 mm. In the case of spherical ends of 1.27 cm radius, impact at a velocity as low as 10 cm/sec. resulted in flattening the ends, the pressure exceeding the elastic limit for steel.

## INTRODUCTION

TWO distinct experiments have been previously reported which led to the conclusion that the separation of two bars, with plane ends, after an end-on collision was due to a local compression in the immediate vicinity of the common surface of contact and not to a compressional wave which traversed the length of each bar, was reflected and returned to the contact ends. The first<sup>1</sup> of these was performed with a slow speed model of colliding bars which consisted of two helical springs with each coil weighted and the colliding ends fitted with brass annular rings. It was found that the springs separated when the compressional wave had traversed but one fourth the length of each spring.

In the second experiment<sup>2</sup> a steel bar was made to strike against another cylindrical piece of steel whose mass equalled the mass of the bar but whose length was only one sixth that of the bar. The duration-velocity curve for this combination was identical with the curve for two similar bars. In general, the nature of all duration-velocity curves indicated that the duration of impact bore a definite relation to the initial velocity of impact and was not a constant for all velocities as predicted by the com-

<sup>1</sup> Tschudi, *Phys. Rev.* 18, 423 (December 1921).

<sup>2</sup> Tschudi, *Phys. Rev.* 23, 756 (June 1924).

pressional wave theory. Wagstaff<sup>3</sup> aimed to show, by the use of bars with rounded ends, that both the compressional wave and local compression enter into the problem, the former predominating in the case of very long bars and the latter alone controlling the process in the case of short bars, i.e., that the shorter the bars the more nearly does Hertz's theory<sup>4</sup> of local compression for colliding spheres hold. The author has found, as will be shown in this paper, that the use of bars with rounded ends proved unsatisfactory because of stresses which exceeded the elastic limit; and further, that for plane ends the duration of impact varies with the area of contact at any given velocity.

These previous experiments suggested the problem of determining the order of the depth of compression. This was the purpose of the present experiments which were performed with copper bars and with steel bars of the same mass with their colliding ends copper plated.

#### THE APPARATUS

The bars were each suspended in much the same manner as in the earlier work,<sup>2</sup> from knife edge supports by two bifilar suspensions. The upper end of each strand of these suspensions terminated at an adjusting screw which permitted a four fold adjustment for each bar. An electromagnetic release held one of the bars, drawn aside, in the proper position from which it could be released at will. The length of time in which an electric current flowed through the bars during a collision determined the duration of the impact. It was found that additional wires, used for current carriers, hindered the motion of the bars and altered the value for the duration of impact. Hence the suspending strands themselves were used to carry the current. The relative initial velocity of impact was calculated from the height through which the deflected bar dropped. (The second bar was kept at rest initially.) This height was determined with a cathetometer which measured accurately to thousands of a centimeter.

In the present experiments an oscillograph was employed for measuring the duration of impact. A special camera which required a five-foot length of film was employed. The peripheral speed of the camera drum was approximately 10 meters per second. No effort was made to damp the element critically, as was done in the earlier experiments because the contact resistance was of no concern here. Since the camera shutter was open for only one revolution of the drum, close coordination was required between the release of the deflected bar and the opening of the shutter.

<sup>3</sup> Wagstaff, *Proc. Roy. Soc. A*105, 544 (1924); also *Phil. Mag.* 48, 147 (1924).

<sup>4</sup> Hertz, *Miscellaneous Papers*, p. 146, 1896.

This was accomplished by the use of a single-pole double-throw switch which in the maximum displacement of the pole was about 2 cm in the vertical. With the pole in the neutral position, the one bar drawn aside, and the camera drum rotating, a catch was pushed aside which allowed the pole to fly upward under the influence of a spring. The circuit containing the electromagnet was thereby closed and the bar released. An instant before the two bars came in contact, the pole was pushed down through the neutral position and the circuit which actuated the camera shutter was closed.

The circuit containing the two bars and oscillograph element contained no inductance, but a resistance of four lamps in parallel was required to protect the element. A two volt cell supplied the requisite current.

### THE EXPERIMENTS

Before any records could be obtained, it was of the utmost importance to adjust the bars carefully. Not only was it necessary that the two bars be horizontal but, far more important, that their colliding ends be parallel. These conditions were obtained by the use of the eight adjusting screws. Adjustments were completed only when no light could be seen through the junction of the colliding ends, with both bars in their equilibrium positions, when observed in two directions perpendicular to each other. The stand of the electromagnetic release was first stationed so as to permit the bar which was to be deflected, to be raised to the desired height and then shifted laterally until its stop and the opposite ends of the bars fell in the same line. This latter adjustment, if properly made, assured a collision in which the colliding ends hit true. When this was not accomplished the oscillogram registered this fact, and a small shift of the stand corrected the fault.

Two satisfactory exposures were obtained for each velocity of impact before proceeding with another velocity. A duration-velocity curve was obtained for a pair of copper bars of length 54.2 cm, diameter 2.54 cm, and mass 2430 gm. A similar curve was obtained for a pair of steel bars of the same diameter and practically the same mass, but of length 61.3 cm. These curves are both given in Fig. 1.

The steel bars were then fitted with copper plugs so that the bars appeared to have a thickness of 0.32 cm of copper on the colliding end of each. The purpose of these plugs was to determine if that thickness was sufficient to yield the same results as those of copper bars. Unfortunately, it was difficult to screw these plugs into the steel bars sufficiently tightly without marring the faces of the plugs. Nevertheless, a series of tests was

made which resulted in a smooth curve that lay far above the copper curve at very small velocities but came close to it at larger velocities.

Since copper cannot be deposited upon steel from a cupric solution it was necessary to deposit a copper base from a cuprous solution. The following recipe was used in preparing the cuprous solution: water, 3.75 liters; sodium cyanide, 64.0 gm; copper cyanide 56.8 gm; ammonium chloride 9.5 gm. Before employing this solution, the customary care was taken to clean thoroughly the ends of the steel bars that were to be plated. The cleaning process consisted in rubbing the surfaces with fine emery paper then dipping them into a boiling solution of concentrated potassium hydroxide, rubbing with scouring powder, dipping again in the alkaline solution and finally rinsing in tap water.

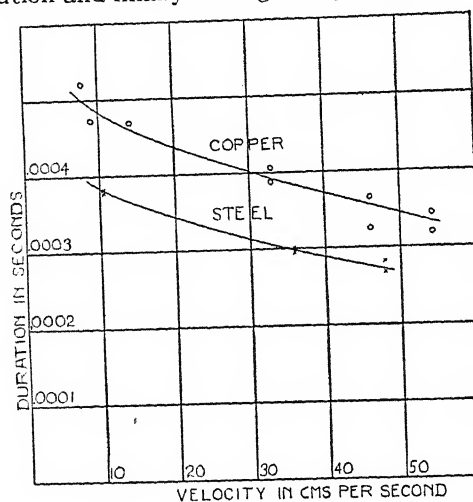


Fig. 1. Duration of impact as a function of velocity of impact, for steel and copper bars.

In the electrolytic bath, the copper anode was flat on the bottom of the vessel. The bar was thrust into the solution sufficiently to wet only the surface to be plated and was clamped in a vertical position. The surface tension of the liquid caused it to climb up the side of the bar about 0.32 cm. A current of 0.1 ampere was sent through the cell for thirty minutes. This length of time was found to be a minimum in order to deposit a sufficient amount of copper to form a base for the deposition from a cupric solution. It was impossible to use the cuprous solution to deposit the requisite thickness of copper because this deposition was found to be of a spongy nature when continued over a period of several hours. The deposition from the cupric solution upon the base from the cuprous solution was, however, of the same smooth, lustrous character as when deposited upon a pure piece of copper.

After removal from the cuprous cell, the plated portion of the bar was cleaned as before with the exception of the rubbing with emery paper. In the cupric cell, a current of .05 ampere was maintained. A copper sulphate solution was used in this cell.

The duration-velocity curve for the bars with the first deposition from the cupric solution is given in Fig. 2, where also the curve for the copper bars is repeated. We have here a comparison of pure copper bars with steel bars with copper plated ends, each having the same mass and diameter, so that the impact relations are practically the same.

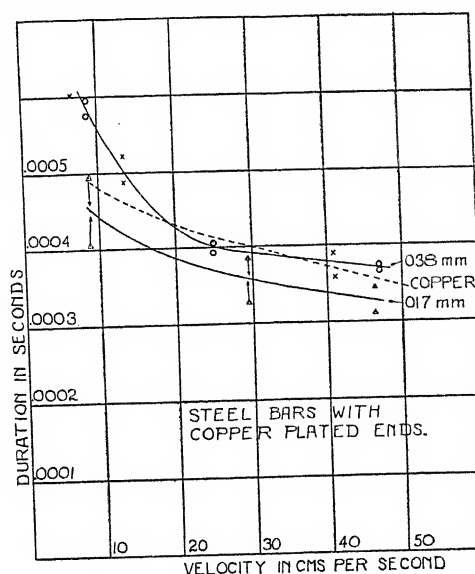


Fig. 2. Effect of plating steel bars with copper, on the duration of impact.

An additional layer of copper was then deposited from the cupric solution, with the purpose of determining whether a thicker layer would produce a duration-velocity curve which lay above the one for the first layer. This, however, was not found to be the case. The points corresponding to the thicker layer are indicated by small crosses in Fig. 2. The closeness of these points to the first curve indicates that the first thickness of copper was sufficient to produce results similar to those of pure copper bars.

The copper deposition was next removed from the steel bars in a lathe. It is worthy to note that the plated copper was found to be firmly fastened to the steel and did not peel off under the tool.

Again the ends of the steel bars were plated from the cuprous solution, but no additional copper was deposited from the cupric solution. Another



series of tests were made. The resultant duration-velocity curve, given in Fig. 2, fell below the curve for pure copper bars but above the curve for steel bars with unplated ends.

In calculating the thickness of copper deposited it was assumed that the form of the deposition was in the shape of a cup 0.32 cm deep with walls and bottom of the same thickness. The first deposit of copper was then computed to have a thickness of .038 mm, the second .064 mm, and the third .017 mm. One can conclude then that the equivalent thickness of deposited copper on steel bars which will give the same impact results as pure copper bars of the same mass and diameter lies between .02 mm and .04 mm.

#### EFFECT OF CHANGE OF CONTACT AREA

The question arose whether or not the duration of impact varied, at any given velocity, for different contact areas. In order to answer this question, the colliding ends of the steel bars were turned down to 1.90 cm for a distance of 0.32 cm back from the end. A duration-velocity curve was then obtained which is given in Fig. 3. The same ends were then turned down to 1.27 cm diameter and another curve obtained which is likewise given in Fig. 3. The curve for the steel bars with diameter 2.54 cm is repeated here. It will be noticed that with a decrease in the common area of contact the duration of impact increases. Evidently the duration of impact of a pair of bars means nothing unless the common area of contact is specified.

The relation

$$t = c_1/d^{1/2} \quad (1)$$

where  $t$  is the duration of impact and  $d$  the diameter of the circular contact area, agrees with experimental curves very well. In the following tables it will be seen that, for any definite velocity,  $c_1$  is nearly constant.

$v=10$		$v=20$		$v=30$	
$d$	$c_1 \times 10^4$	$d$	$c_1 \times 10^4$	$d$	$c_1 \times 10^4$
2.54 cm	6.12	2.54 cm	4.57	2.54 cm	4.94
1.90	5.85	1.90	4.80	1.90	4.96
1.27	6.19	1.27	5.32	1.27	5.02

Likewise, for any given contact area, the relation

$$t = c_2/v^{1/5} \quad (2)$$

holds admirably for all cases. This form of the velocity function has been agreed upon by all investigators, whether they used spheres, bars with rounded ends, or bars with plane ends. Combining (1) and (2) we have

$$t = A/d^{1/2}v^{1/5} \quad (3)$$

The coefficient  $A$  is not a universal constant, but varies with the substance. Its values for steel and copper are  $9.7 \times 10^{-4}$  and  $12.35 \times 10^{-4}$  respectively, in c.g.s. units.

The steel bars were next rounded so as to have a hemispherical surface of 1.27 cm radius. Upon allowing the bars to collide, it was noticed that the clear metallic ring which had accompanied all previous collisions with plane ends, was lacking, and instead that a dull thud sounded as though two bars of lead had collided. Examination of the rounded ends showed a small flat area of about 1/2 mm diameter, indicating that the elastic limit had been exceeded and the ends of the bars had been mashed in. This occurred at the smallest velocity at which measurements were made. Successive blows at the same velocity increased the area of the

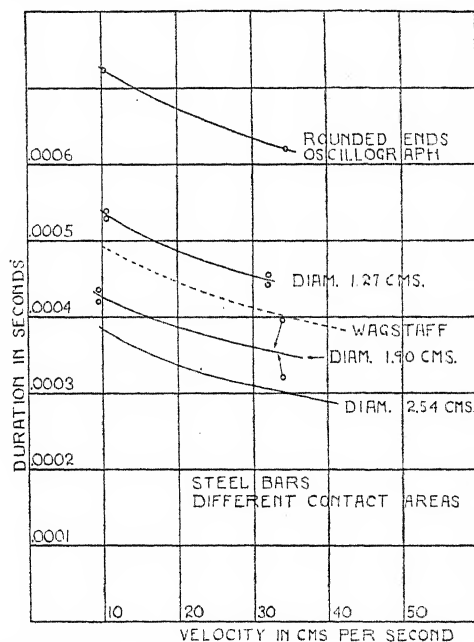


Fig. 3. Effect of contact area on duration of impact.

flattened portion. Examination of the oscillograms showed that there was no definite point at which the current had broken and therefore no measurement of the duration of impact could be made. A condenser method for measuring the duration of impact would not have disclosed the fact that the impact had been erratic, which emphasizes the necessity of an oscillograph for making measurements of this kind.

The bars were again rounded so as to expose unstrained surfaces and allowed to collide at the same velocity as before. Three successive

collisions were recorded. The resultant oscillograms proved satisfactory this time. The duration of impact, as measured from them, was found to grow smaller as the number of impacts increased, due, no doubt, to the increase in contact area. Similar results were obtained at a greater velocity. They are tabulated below.

$v = 10.28$		$v = 34.80$	
Trial	Duration	Trial	Duration
1	$7.23 \times 10^{-4}$ sec.	1	$6.20 \times 10^{-4}$ sec.
2	6.82	2	5.32
3	5.75	3	4.35

The durations of impact for the first trial at each of the two velocities are plotted in Fig. 3. In the same figure is plotted a broken curve for steel bars, of practically the same dimensions, from values given by Wagstaff,<sup>3</sup> who used a condenser discharge method for measuring the duration of impacts.

In the classical relation between the impulse and change in momentum of colliding bodies, if it be assumed that the force during the impact varies as  $F = B \sin (\pi t/t_1)$  where  $t_1$  is the duration of the impact, then it can readily be shown that the maximum force exerted during impact is  $B = (mv - mu)\pi/2t_1$ . Substituting values from the preceding table, for example,  $t_1 = 7.23 \times 10^{-4}$ ,  $v = 10.28$ , we have  $B = 5.22 \times 10^7$  dynes. This force is distributed over an area of  $1.96 \times 10^{-3}$  cm.<sup>2</sup> Hence the force per unit area is computed to be  $2.66 \times 10^{10}$  dynes, more than twice the maximum limit of elasticity tabulated for steel.

The author is greatly indebted to the Bureau of Standards for the loan of the oscillograph used in these experiments and takes this opportunity to express his thanks and obligation. Suggestions and criticisms offered by Dr. J. S. Ames during the course of the experiments were of high value and greatly appreciated.

JOHNS HOPKINS UNIVERSITY  
March 18, 1925.

INTERFERING EFFECT OF TONES AND NOISE  
UPON SPEECH RECEPTION

BY VERN O. KNUDSEN

## ABSTRACT

The interfering effect upon speech of tones and noise was measured by determining the percentage of vowel, consonant and word articulations correctly heard by an observer who listened in the presence of a tone or noise to meaningless monosyllables spoken at a distance of 2 meters. The interfering tones varied in pitch by octaves from  $C_2$  (128 d.v.) to  $C_7$  (4096 d.v.) and in loudness from slightly above minimal audibility to near the painful limit. The interfering effect increases with increasing loudness of tone or noise at an accelerated rate; for tones with a loudness less than the loudness of the speech, the effect is almost independent of the pitch, but as the interfering tone becomes louder, the tones of lower pitch produce a relatively greater and greater interference. These results are consistent with the auditory masking data of Fletcher, Wegel and Lane. A noise produces twice the interfering effect of a tone of the same loudness. These results indicate that for good hearing in an auditorium the speech energy should be from 1000 to 10,000 times the energy of any interfering noises, and that sound-absorbent materials for the reduction of noises in auditoriums should absorb equally tones of all pitches below  $C_7$ . Some experiments with rather deaf persons will be reported elsewhere.

THE work described in this paper is part of a larger program, the object of which is to determine quantitatively the influence of the various factors which affect the quality of speech in an auditorium. The specific object of the present problem, as the title suggests, is to determine (1) the relative interfering effect upon speech of tones of different pitch and loudness, and (2) the interfering effect upon speech of typical noises of different loudness.

Telephone engineers have done considerable work upon the interfering effect of noise upon speech transmitted over various types of telephone circuits. Up to the present, however, there has been very little published upon the subject. The work of the writer differs from the work done by telephone engineers in that the writer's tests are conducted in a typical small auditorium, and the observer listens directly to the voice of the speaker rather than to the speaker's voice transmitted over a telephone circuit.

The tests were all conducted in a room having a volume of 15,000 cubic feet and a period of reverberation of 1.3 seconds. The interfering tone or noise was conducted to the observer's ears by means of a pair of telephone receivers which were adjusted so that each receiver was at a fixed distance

of 2 cm from the ear to which it was attached. The speaker, or "caller," spoke with a natural, easy, conversational voice, at a distance of two meters from the observer. The energy of the speech reaching the observer was slightly less than  $10^5$  times the minimal audible speech energy. Preliminary comparisons of the loudness of the speech with the loudness of tones of which the energy could be accurately determined, indicated that the loudness of the speech was approximately 47 logarithmic units.<sup>1</sup> This loudness of speech is comparable with the loudness of speech in an average auditorium.

The measurements were made by the usual method of articulation tests commonly used in testing the transmission efficiency of a telephone circuit. The "caller" called out meaningless consonant-vowel, vowel-consonant and consonant-vowel-consonant monosyllables, and the observer recorded what he heard, or thought he heard. By comparing the observer's lists with the lists called, the number and nature of the errors can be determined. The results of such tests are expressed as the percentage vowel articulation, the percentage consonant articulation, and the percentage "word" articulation.

The total number of speech-sounds called in making these tests was 29,000. These speech-sounds or "words" were called in groups of three, at the rate of one speech-sound each .85 of a second. Tests were made with interfering tones of  $C_2$  (128 d.v.),  $C_3$  (256 d.v.),  $C_4$  (512 d.v.),  $C_5$  (1024 d.v.),  $C_6$  (2048 d.v.), and  $C_7$  (4096 d.v.). Tests were also made with a typical noise as the interfering source. The interfering tones and the noises were maintained at various loudness levels, ordinarily at 20, 40, 60 and either 70 or 80 log-units. After many tests had been completed it was obvious that it was superfluous to take measurements below 40 log-units. 400 speech-sounds were called for each condition tested. Half were called by the writer, and the other half by an assistant. The observer and caller changed positions four times during the tests of each interfering condition. The tests with the same interfering source also were distributed over at least four different periods of observation. This would tend to make all of the results more nearly comparable. An indication of the uniformity of the speech and hearing of the two observers is the fact that the average percentage word articulation of one observer,

<sup>1</sup> This unit of loudness, proposed by telephone engineers, is very convenient. The loudness of the tone, expressed in this unit, is ten times the logarithm to the base ten of the ratio of the energy of the tone to the energy of a barely audible tone of the same pitch. For example, a tone whose energy is one million times the energy of a barely audible tone of the same pitch, is 60 log-units.

for the entire series, differed only two percent from the average of the other observer.

Results of the tests are shown in a series of curves, Figs. 1 to 3. Fig. 1 shows the results of the tests with tones as the interfering source. The percentage articulations for vowels, consonants and words are plotted as

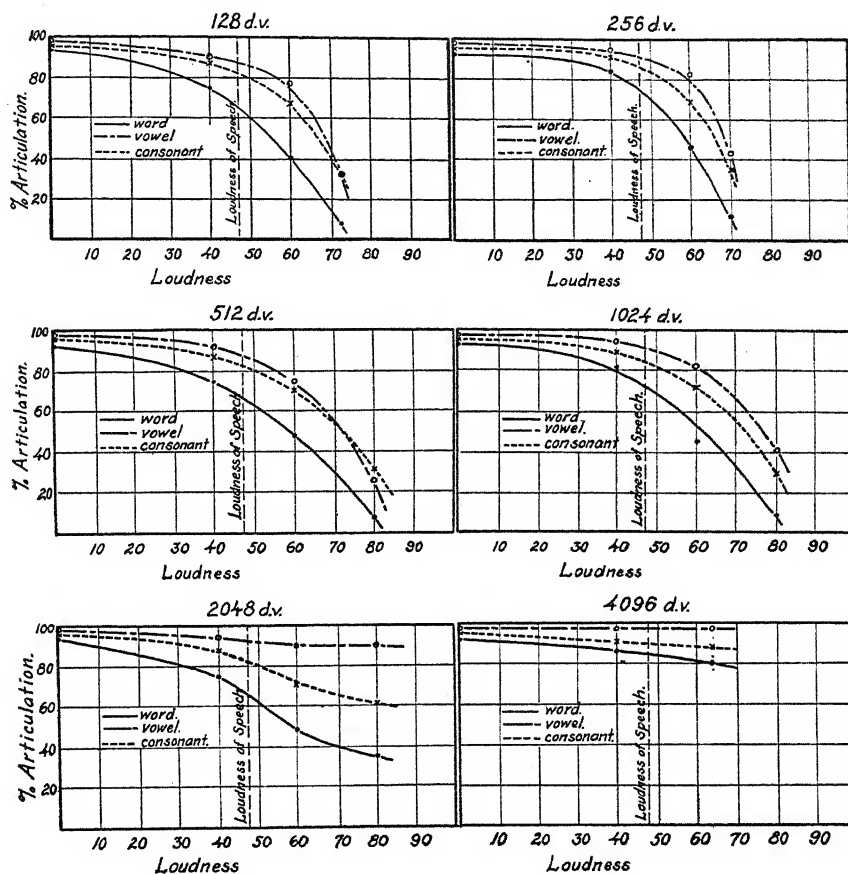


Fig. 1. Interfering effect of tones.

a function of the loudness. Fig. 2 shows the results obtained with a noise consisting of a series of clicks in the telephone receivers, produced by interrupting a current flowing through an inductance in series with the telephone receivers. Curve (1) expresses the word articulation when the frequency of the clicks was 14 per second; curve (2) the word articulation when the frequency of interruption of the clicks was 20 per second. Fig. 3 indicates how the percentage articulations for vowels, consonants and words varied with the pitch of the interfering tone, at two different loud-

ness levels, viz., 47 log-units, the loudness of the speech, and 70 log-units.

The conclusions which may be drawn from the data are as follows.

1. The interfering effect of tones of which the loudness is less than the loudness of the speech, is almost independent of the pitch of the tones. However, for very high tones, above  $C_6$  (2048 d.v.) the interfering effect seems to decrease as the pitch rises, so that tones above  $C_7$  (4096

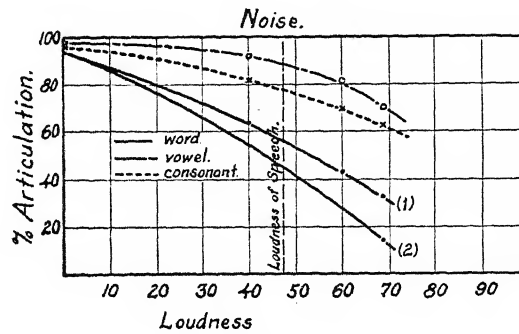


Fig. 2. Interfering effect of noise.

d.v.) should have practically no interfering effect. A tone of any pitch below  $C_6$ , equal in loudness to the speech loudness, reduces the word articulation to about seventy percent. This may be seen from an inspection of Fig. 3.

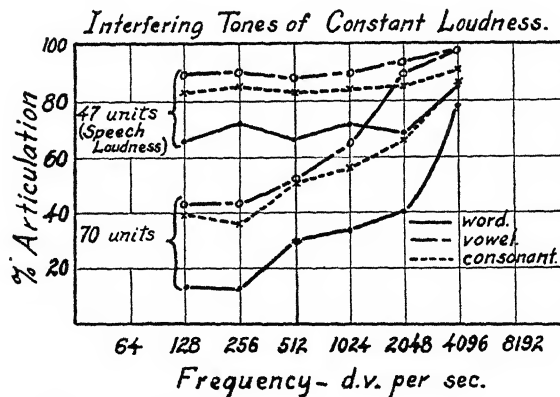


Fig. 3. Variation of interfering effect with frequency.

2. The interfering effect of tones whose loudness is greater than the loudness of the speech depends very much upon the pitch of the tones, decreasing markedly as the frequency increases. For example, at 70 log-units, the vowel, consonant and word articulations for  $C_3$  (256 d.v.) are 43 percent, 36 percent and 13 percent, and for  $C_7$  (4096 d.v.) are 98



percent, 85 percent and 78 percent, respectively. This conclusion is consistent with the data of Fletcher, Wegel and Lane on the auditory masking of one tone upon another. As the interfering tones become louder, the non-linear response of the ear's mechanism introduces many combinational or "subjective" tones, all of which are higher in pitch than the fundamental. Hence, as tones of low pitch become louder, they introduce many combinational tones which will lie within the important speech range. On the other hand, the tones of high pitch will introduce combinational tones of which most will be above the important speech range; therefore, when the loudness of these tones is increased, the interfering effect does not increase nearly as rapidly as it does with an increasing loudness of low tones. These results are clearly indicated in Fig. 3. It is to be noted therefore that the interfering effect of the low frequency components of noises, provided the noises are loud, is greater than the interfering effect of the high frequency components.

3. The interfering effect of tones and noises, generally, is felt more in relation to consonants than to the vowels. However, low pitched interfering tones reduce the consonant articulation only slightly more than they do the vowel articulation, whereas high pitched tones reduce the consonant articulation very much more than they do the vowel articulation.

4. A noise produces a greater interfering effect than a tone of any pitch. Thus a typical noise, of loudness equal to the loudness of the speech, reduces the word articulation to about fifty percent, whereas any tone below  $C_6$  (2048 d.v.) of the same loudness, reduces the word articulation to only about seventy percent.

5. From an inspection of Fig. 2 it will be seen that even a little noise reduces the word articulation appreciably. Roughly, it may be concluded that the speech must be at least 30 or 40 log-units louder than the noise if the noise is not to produce a harmful effect. Expressed in energy, the energy of the speech should be from 1000 to 10,000 times the energy of the interfering noises. This indicates the necessity for extreme reduction of noises in any auditorium.

6. A practical conclusion indicated by these data is that sound-absorbent materials for the reduction of noises in architectural interiors should absorb equally, tones of all pitch below  $C_7$  (4096 d.v.). This, of course, is also desirable from the standpoint of having no distortion of speech or music.

Similar experiments, conducted with certain rather deaf individuals who claim they hear better in the presence of a noise, indicate that they

actually hear not as well in the presence of a noise.<sup>2</sup> These experiments, together with other experiments and explanations pertaining to this problem, will be presented in a future paper.

The writer wishes to acknowledge the assistance of Mr. W. A. Munson and Mr. F. L. Poole. He also wishes to express his thanks for the use of articulation lists which were furnished through the courtesy of Dr. Harvey Fletcher of the Western Electric Company.

DEPARTMENT OF PHYSICS,  
UNIVERSITY OF CALIFORNIA,  
SOUTHERN BRANCH.  
April 7, 1925.

<sup>2</sup> Kranz and Fletcher have published some plausible reasons why certain of such people have an advantage over normally hearing individuals in the presence of a noise. See F. W. Kranz, *Laryngoscope*, March, 1924, and H. Fletcher, *Volta Review*, September, 1924.

## BOOK REVIEWS

**Die meteorologischen Messmethoden.** WALTER GEORGII.—The fifty-eight octavo pages of this work constitute a section of the *Handbuch der biologischen Arbeitsmethoden* (Abt. II, Heft 4, Lief. 118) now appearing under the general editorship of Dr. Emil Abderhalden, with the assistance of 500 noted specialists.

Nothing is said about the measurements of the total intensity of insolation, nor its spectral distribution; nothing about sky brightness nor sky polarization; nor anything about the electrical state of the atmosphere. Some of these things, perhaps all, are to be discussed by other specialists.

Naturally, German instruments and German practice are stressed. American variations from either are given but little or no attention. In the main, however, that is not important, since in meteorology, as in other sciences, the exact manner of getting data is of no consequence so long as they are reliable.

Among the various thermometers described is one for measuring sunshine. This consists of a vacuum-jacketed black bulb thermometer in conjunction with a similarly jacketed clear bulb instrument. Of course the two individuals of this pair give different readings when exposed to sunshine, but the use, biological or otherwise, one can make of that difference is not obvious. This is one of the instruments we in America do not use. We prefer the pyrheliometer, for instance, which gives interpretable readings.

The measurements of atmospheric pressure, humidity, wind velocity and direction, precipitation, and other meteorological elements, are simply explained, and many of the instruments mentioned satisfactorily illustrated. Under evaporation, however, only one type of instrument is described, and that an unfamiliar one, at least to American meteorologists.

In short, the descriptions here given of meteorological instruments and their uses are very good, for the class of readers addressed, that is, those who use instruments merely as purchased tools for the collection of approximately accurate data. The book, or chapter rather, has its place, and fills it very well.—Urban and Schwarzenberg, Berlin and Vienna, 1924.

W. J. HUMPHREYS

**Zeemaneffekt und Multiplettstruktur der Spektrallinien.** E. BACK and A. LANDÉ.—This is the first of a series of monographs, prepared under the editorship of Professors Born and Franck, which aim to cover the various divisions of the modern theory of the structure of matter in fuller detail than can be done in a single book. Its scope is confined strictly to the topics indicated by its title (excluding even such closely related matters as the Stark effect and the formulas for spectral series) and within this field it is authoritative, precise, and complete.

The theoretical section (prepared by Professor Landé) covers so much ground in a hundred pages that it is hard reading for the novice—harder, indeed, than the original papers from which it is condensed. The available space, however, could hardly be better used. The normal and anomalous Zeeman effects, the structure of multiplets, and the interval and intensity rules are very clearly discussed; then the more complicated relations which appear in spectra "*zweiter stufe*" such as that of neon; and finally the Paschen-Back effect, the magneton theory and the recent "relativistic" formulas for the separations of the multiple terms. Half-quantum numbers are introduced freely; the anomalous Zeeman separations formally explained by the assumption that the magnetic energy of the central part (Rumpf) of the atom, is to be counted twice; and the relativistic interpretation of the optical term-separations dismissed as incredible, in view of other evi-

dence. The need for a fundamental modification of existing theory, to account for these and other difficulties, is clearly stated.

The experimental part (written by Dr. Back) gives in much more detail an excellent account of the admirable technique developed at Tübingen for the study of the Zeeman effect. With an intermittent vacuum arc in a field of 38,000 gauss an actual resolving power of more than 250,000 has been attained in the spectra both of solid electrodes and of gases. The various types of complex Zeeman patterns and the methods by which these are analysed are fully described and illustrated by numerical examples and by a series of excellent photographic reproductions of original negatives.

A valuable bibliography of the subject, up to about the middle of 1924, and a table of the theoretical Zeeman patterns for systems from the doublets to the septets, complete the volume. The usefulness of the last table is impaired by the fact that it includes only the *sp*, *pd* and *df* combinations. When a second edition of the work (which the rapid advance of this field must soon demand) appears, it is to be hoped that the *g*, *h*, and *i* combinations which occur in the more complex spectra, will be included, and also those of types *pp'*, *dd'*, etc., and also that space may be available for a fuller discussion of the theory. The high price of the book might indeed have permitted the allotment of this space in the present edition.—Pp. xii+213. Julius Springer, Berlin, 1925. Unbound M 14.40; bound M 15.90.

H. N. RUSSELL

**Théorie Mathématique de l'Électricité**, TH. DE DONDER.—In all of the changes that are taking place in our conceptions of the physical universe, Maxwell's system of equations for stationary media has so far held its own, and a consistent development of these equations, based upon the minimum number of special assumptions, is particularly welcome at the present time. Professor deDonder, of the University of Brussels, has written an excellent book, with this object in view.

Electricity is regarded as having a real existence in euclidean space. The electric potential is defined in the usual way for point, surface and volume distributions. Electric force is *defined* as the negative gradient of the potential. The electric resultant, on the other hand, is defined, with the aid of Coulomb's experimental law, as the mechanical force acting on a unit point charge. In the case of surface distributions, for points on the surface, and inside polarised distributions, these definitions lead to different results. The behavior of the potential, together with its first two derivatives, at bounding surfaces is much more fully treated than in most of the modern text-books. The author's treatment of polarised distributions, both throughout volumes and over surfaces, and his use of the vector potential in this connection, is worthy of particular note.

Electric currents are defined as electric charges in motion. Corresponding to volume and surface charges, there are volume and surface currents. Magnetic force is *defined* as the curl of the vector potential due to electric currents. In this way it is possible to develop the theory of magnetism without assuming the existence of real magnetic poles. For this purpose it is necessary to appeal to experiment, in the law, attributed to Laplace, according to which the mechanical force exerted upon a current element in a magnetic field, is proportional to the vector product of the current element and the magnetic force. In order to bring magnetic polarisation into the general scheme, it is shown that a closed current is equivalent in its effects to a magnetic doublet formed of two equal and opposite fictive magnetic poles. The author's treatment of electric polarisation is such that by a mere change of expression it applies equally well to the magnetic case. This analogy is aided by his notation; Roman letters are used for the electric quantities and script letters for the corresponding magnetic quantities.

The final book in this volume deals with the variable electromagnetic field and Maxwell's equations. The continuity of electric currents leads to the introduction of displacement currents and the first of the triads of Maxwell; Faraday's experimental

law of induced electromotive force leads to the second triad. Poynting's theorem is developed in all generality so as to include the energy dissipated in dielectric and magnetic hysteresis; and it is shown how the forces in an electric field may be interpreted with the aid of stresses in a medium.

Professor de Donder has in this admirable book made a valuable contribution to physical science. The appearance of the second volume, to include applications to the theory of electrons and electric waves, and, it is to be hoped, to bodies in motion, will be awaited with interest.—Pp. 198, Paris, Gauthier-Villars, 1925. E. P. ADAMS

**Lehrbuch der Technischen Physik. Masse und Messen, Mechanik, Akustik, und Thermodynamik.** GEORG GEHLOFF, editor.—This book is another product of the recent rapid development in Germany of technical physics, which has already resulted in the founding of the Deutschen Gesellschaft für Technische Physik and the Zeitschrift für Technische Physik. The book is ostensibly addressed to advanced students and engineers, but will be found of interest by many experimenters in pure physics because of the many descriptions of technical processes which may be adapted to experimentation. Furthermore it will be found a valuable book of reference in those subjects which it covers, because it contains in an astonishingly short space most of the essential theory and many of the essential facts. The condensation is so great, in fact, that the German advanced student or engineer must be recognized to be a different breed from that raised in this country if he can be successfully taught from this as a text book.—Pp. xiii + 386, Johann Barth, Leipzig, 1924. P. W. BRIDGMAN

**Transmission Circuits for Telephonic Communication.** K. S. JOHNSON.—The purpose of the author has been to cover the general theory and principles which are applicable to the development and design of circuits and lines for association with such telephonic instruments as transmitters, receivers, and vacuum tubes. The detailed characteristics of these instruments are not discussed. Familiarity with elementary alternating current theory and complex-quantity notation is assumed; but a review of the latter, with condensed formulas, is given in one of the seven mathematical appendices.

While there are many admirable books dealing with power transmission, there has long been a need for a book dealing with the fundamental principles of telephonic circuits. The treatment is comprehensive and masterly, being of particular value to the specialist and to one whose training qualifies him to appreciate analysis in this particular field.—Pp. 326. Price \$5.00. D. Van Nostrand Co., 1925. FREDERICK BEDELL

**Der Radio-amateur.** P. LERTES.—This book would be of interest in parts to all amateurs. It begins with a discussion of the elements of electric circuits and electricity, covers very briefly and generally all the principal methods of transmitting and receiving, both telegraphy and telephony. It is non-mathematical. Some curves are shown to explain what the author considers important parts of theory. Numerous circuits are given as well as many photographs of apparatus.

Too large a part of the book is taken up with elementary electricity and with obsolete transmission systems to make it of value to a technical man who wishes to turn radio amateur. As it stands, the remainder would satisfy the type of amateur that we know in the United States or the physicist who knows nothing of radio and wants some elementary book on the subject, but it is hardly suitable for one who wishes to build his own apparatus.

An appendix contains tables of time signal transmission, telegraphic and broadcasting schedules, and other items of interest to the amateur.—Pp. 214, figs. 114. Theodor Steinkopff, Dresden and Leipzig, 1924. R. A. HEISING

**A Laboratory Manual of Experiments in Physics.** LEONARD ROSE INGERSOLL.—This manual is the outgrowth of one used for many years in the University of Wisconsin in connection with the elementary courses. The 76 experiments described are for the most part standard but are well selected and include such experiments as the study of centrifugal force by means of motor driven rotating balls held in by springs, the determination of the mechanical equivalent of heat by letting shot fall repeatedly from one end to the other of a long wooden tube, the measurement of heat conductivity of several insulating materials, study of the vertical distribution of light and the efficiency of an incandescent lamp, and a study of the eye as an optical instrument with the aid of a model. The directions and notes are clear and yet concise, the result of considerable practical experience with many students. The book is well printed and illustrated and should be useful in any laboratory which has not its own printed manual of instructions.—Pp. 220, 56 fig., McGraw-Hill, New York, 1925. \$2.00. G. S. F.

**The "Chemical Age" Chemical Dictionary.** This dictionary defines in an elementary way about 2000 of the more common chemical terms, and is intended to meet the needs of those who have occasion to consult any chemical abstracts or articles. It is said to be the forerunner of successive volumes on "Organic Substances," "Inorganic Substances" etc. It seems expensive for its size.—Pp. 158, Van Nostrand Co., New York. Printed in Great Britain, 1924. \$4.50. G. S. F.

**Discours de la Nature de l'Air etc.** EDME MARIOTTE.—This is one of the collection of memoirs and works in the series "Les Maitres de la Pensée Scientifique" published by Gauthier-Villars. It includes a brief biographical notice and besides the *Discours de la Nature de l'Air*, letters on "La Vegetation des Plantes" and "Nouvelle Découverte Touchant la Vue."—Pp. 118. 3 fr. Gauthier-Villars, Paris. G. S. F.

# THE PHYSICAL REVIEW

## THE ENERGIES OF MULTIPLE X-RAY IONIZATION OF LIGHT ATOMS

BY LOUIS A. TURNER\*

### ABSTRACT

The assumption is made that the removal of a K electron has the same effect on the energies of the outer electrons of the atom as the increase of the nuclear charge by one unit. The energy for the successive removal of a K electron and an L electron is computed for elements Na to K on this basis. By means of Wentzel's theory and Hjalmar's measurements of the K spark lines  $a_3, a_4, a_5, a_6$ , other multiple ionization levels are computed for the elements Na to S. The square roots of the energies ( $\sqrt{\nu/R}$ ) for the successive removal of the first, second, and third L electrons plotted against atomic numbers give three parallel straight lines indicating that the removal of the first L electron reduces the screening constant (7.27) for the remaining ones by 0.62, and that the removal of the second one causes a further reduction of 0.65. Similar lines are obtained for the two K electrons, the screening constant (1.5) being reduced 0.16 by the removal of the first one. The energies for the successive removal of two electrons from a helium-like ion made up of a nucleus of charge  $Z$  and two electrons are computed for these atoms. The plot indicates that the experimental value of the *K absorption limit of phosphorus* is in error.

SEVERAL experimenters have found weak lines accompanying the K emission lines of some of the light elements, which do not correspond to transitions between levels of the ordinary scheme of x-ray levels. They are all of shorter wave-length than the strong lines which they accompany. Wentzel<sup>1</sup> has advanced the theory that these lines are emitted by multiply ionized atoms, and are thus analogous to the spark lines of optical spectra. Adopting Wentzel's notation,  $K^p L^q$  will be used to indicate the term value equivalent to the energy of an atom which has had  $p$  electrons removed from the K shell and  $q$  electrons removed from the L shell. The following equations indicate the transitions which are thought to give rise to the different observed lines, the wave-number of the line being equal to the difference between the wave-numbers of the terms corresponding to the

\* National Research Fellow.

<sup>1</sup> G. Wentzel, Ann. der Phys. 66, 437 (1921); 73 647 (1924).



two states involved. They are arranged in the order of increasing wave-number.

$$\begin{aligned}
 a_1 &= K - L \text{ (the ordinary } K\alpha \text{ doublet, unresolved)} \\
 a_3 &= KL - L^2 \\
 a_4 &= K^2 - KL \\
 a_5 &= KL^2 - L^3 \\
 a_6 &= K^2L - KL^2
 \end{aligned} \tag{1}$$

Of great importance is the fact that the difference between  $a_6$  and  $a_4$  for one element is equal to the difference between  $a_3$  and  $a_1$  for the element of next higher atomic number. That is,

$$(a_6 - a_4)_Z = (a_3 - a_1)_{Z+1}$$

Substitution of the term values given by Eqs. (1) gives

$$(K^2L - K^2)_Z - (KL^2 - KL)_Z = (KL - K)_{Z+1} - (L^2 - L)_{Z+1} \tag{2}$$

Each of these expressions in parentheses is the energy for the removal of one L electron from an atom, those on the left being for atoms of atomic number  $Z$  which have already had two K electrons or one K and one L electron removed, respectively, and those on the right for atoms of atomic number  $Z+1$  which have already had one K electron or one L electron removed, respectively. The equation indicates that the absence of a K electron in the atoms of atomic number  $Z$  is equivalent to the increase of the nuclear charge by one unit, or, in other words, that the screening effect of a K electron is unity and the energy of the L electrons is determined by the difference between the nuclear charge (in electron units) and the number of K electrons surrounding the nucleus. This explanation was given by Wentzel.<sup>1</sup> All of these spark lines result from the jump of one electron from an L orbit (K state of the atom) to a K orbit (L state of the atom), as does the  $K\alpha$  line. The electron orbits involved are, therefore, presumably of the same type as those which give as end states of the  $K\alpha$  transition the  $L_{21}$  and  $L_{22}$  states of the relativity doublet, which for the atoms of low atomic number are too close together to be separated. These are the orbits which are now thought to be analogous to the  $p_1$  and  $p_2$  orbits of optical doublet spectra. For the total quantum number 2 of the L orbits, they are  $2_2$  orbits which are approximately circular and do not penetrate within the orbits of the K electrons, hence the perfect screening by the K electrons would be expected. One might expect small differences between an atom with a K electron removed and one with a nuclear charge greater by one because the two would not be exactly equivalent for electrons whose orbits pene-

trate within the K orbits; the mutual screening of the L orbits would be slightly different, and the energy of a non-penetrating orbit slightly different. Wentzel's explanation amounts to assuming that because Eq. (2) is true, the corresponding terms on the two sides of it are individually equal, i.e., that

$$(KL^2 - KL)_Z - (L^2 - L)_{Z+1} = 0 \quad \text{and} \quad (K^2L - K^2)_Z - (KL - K)_{Z+1} = 0$$

Eq. (2) would hold if these two differences were both equal to any other value. The above considerations show, however, that the assumption that they are equal to zero is in agreement with our present ideas concerning the structure of the atom. Furthermore, if the first of these differences were not equal to zero it would be highly improbable that the second one should have the same value. The screening effect of the second electron, the first one being gone, if not perfect, would probably not be exactly equal to that of the first one while both are present.

Making the assumption that the energy of removal of an L electron depends only upon  $Z - x$ , where  $x$  is the number of K electrons present, it is possible to calculate all of these multiple ionization terms from the ordinary  $K$  and  $L$  terms and the  $a_3$ ,  $a_4$ ,  $a_5$  and  $a_6$  lines. The  $KL$  term is obtained by the addition of the  $K$  term for the atom in question and the  $L$  term of the atom of next higher atomic number, corresponding to the successive removal of the K and L electrons. A slight error is introduced because of the change of the energy and screening effect of the added valence electron of the atom of higher atomic number.  $(KL)_Z = K_Z + L_{Z+1}$ , and then by Eqs. (1),  $(K^2)_Z = (KL)_Z + (a_4)_Z$ , and  $(L^2)_Z = (KL)_Z - (a_3)_Z$ . In a similar way  $(KL^2)_Z = K_Z + (L^2)_{Z+1}$ , and then  $(K^2L)_Z = (KL^2)_Z + (a_6)_Z$  and  $(L^3)_Z = (KL^2)_Z - (a_5)_Z$ . These last three levels can also be computed in a different way for by our assumption  $(K^2L)_Z = (K^2)_Z + L_{Z+2}$ . The equation which expresses the fact that these two methods of computing these levels give the same results, obtained by equating the two expressions for  $(K^2L)_Z$ , is  $(K^2)_Z + L_{Z+2} = (KL^2)_Z + (a_6)_Z$ . It reduces to the equation  $(a_6 - a_4)_Z = (a_3 - a_1)_{Z+1}$  which, as mentioned above, is confirmed by experiment.

The K levels for these elements are given by Fricke's<sup>2</sup> measurements of the K absorption limits. The L absorption limits have not been measured<sup>3</sup> but can be computed from the differences between the wave-

<sup>2</sup> H. Fricke, Phys. Rev. **16**, 202 (1920).

<sup>3</sup> My attention has been called to some new measurements of the L absorption limits, by an improved electrical method, by Holweck (C. R. **180**, 658, 1925). His mean value for Al agrees with the one computed below, but his mean values for the elements from Si to A are 0.2-0.3 greater than the values computed below. The reason for this discrepancy is not apparent.

numbers of the K limits and of the  $K\alpha$  lines measured by Hjalmar<sup>4</sup> and Siegbahn and Dolejšek.<sup>5</sup> If the square roots of these computed L levels be plotted as ordinates with atomic numbers as abscissas a straight line can be drawn through all of the points except the one for phosphorus. The P point also deviates from the similar line for the K levels. If, however, the L level for P be computed from the  $\sqrt{L}$  line and a corresponding new K limit computed by adding  $K\alpha$  to it, the point corresponding to this new K limit will lie on the  $\sqrt{K}$  line. This would seem to be good evidence that there is an error in the determination of the K absorption limit of P. The L limits for Na, Si, and A and the K limits for Na and Si have been obtained in this way. Table I gives Fricke's measurements of the K limits, the measured  $K\alpha$  lines, the computed K and L terms (terms in parentheses having been obtained by interpolation), and the frequencies of the spark lines (measured by Hjalmar<sup>4</sup>). All levels and frequencies are expressed in  $\nu/R$  units. Table II gives the

TABLE I

Z	Element	K(Fricke)	$K\alpha$	K(calc)	L(calc.)	$a_3$	$a_4$	$a_5$	$a_6$
11	Na	.....	76.68	(78.84)	(2.16)	77.21	77.34	.....	.....
12	Mg	95.81	92.35	95.81	3.46	92.99	93.11	93.65	93.83
13	Al	114.67	109.53	114.67	5.14	110.26	110.41	111.05	111.27
14	Si	.....	128.18	(135.19)	(7.01)	129.02	129.18	129.92	130.12
15	P	158.26	148.37	(157.59)	(9.22)	149.33	149.51	.....	.....
16	S	181.81	169.97	181.81	11.84	171.02	171.23	172.68(?)	.....
17	Cl	207.84	193.14	207.84	14.70	.....	.....	.....	.....
18	A	235.73	.....	235.73	(17.95)	.....	.....	.....	.....
19	K	265.33	243.85	265.33	21.35	.....	.....	.....	.....

TABLE II

Z	Element	$K^2$	$KL$	$L^2$	$K^2L$	$KL^2$	$L^3$
11	Na	159.64	82.30	5.09	164.78	86.80	.....
12	Mg	194.06	100.95	7.96	201.06	107.23	13.58
13	Al	232.09	121.68	11.42	241.33	130.06	19.01
14	Si	273.59	144.41	15.39	285.41	155.29	25.37
15	P	318.94	169.43	20.10	333.64	183.08	.....
16	S	367.74	196.51	25.49	385.69	213.01	40.33(?)

values of the multiple ionization levels computed in the way described above. Wentzel stated that Siegbahn had written to him that he had found an absorption limit for S of wave-length somewhat less than half that of the ordinary K limit. It is presumably the  $K^2$  limit corresponding to the simultaneous removal of the two K electrons. I have been unable

<sup>4</sup> E. Hjalmar, Zeits. f. Phys. 1, 439 (1920).

<sup>5</sup> M. Siegbahn and V. Dolejšek, Zeits. f. Phys. 10, 159 (1922).

to find any further published account of that experiment so as to compare the experimental value of the limit with the one given in Table II.

TABLE III

$Z$	Element	$K$	$(K)_2$	$L$	$(L)_2$	$(L)_3$	$K_2'$	$E_2$	$K_1'$
11	Na	78.84	80.80	2.16	2.93	.....	121.19	40.39	.....
12	Mg	95.81	98.25	3.46	4.50	5.62	144.27	46.02	136.20
13	Al	114.67	117.42	5.14	6.28	7.59	169.37	51.95	160.69
14	Si	135.19	138.40	7.01	8.38	9.98	196.50	58.10	187.14
15	P	157.59	161.35	9.22	10.88	.....	225.66	64.31	215.69
16	S	181.81	185.93	11.84	13.65	14.84	256.85	70.92	246.11

$L^2 - L = (L)_2$ , the energy necessary for removal of the second L electron, and  $L^3 - L^2 = (L)_3$ , the energy necessary for removal of the third electron. Similarly,  $K^2 - K = (K)_2$ . These values are given in Table III. As would be expected,  $(K)_2 > K$ , and  $(L)_3 > (L)_2 > L$ . If the square roots of these L values be plotted against atomic numbers three parallel straight

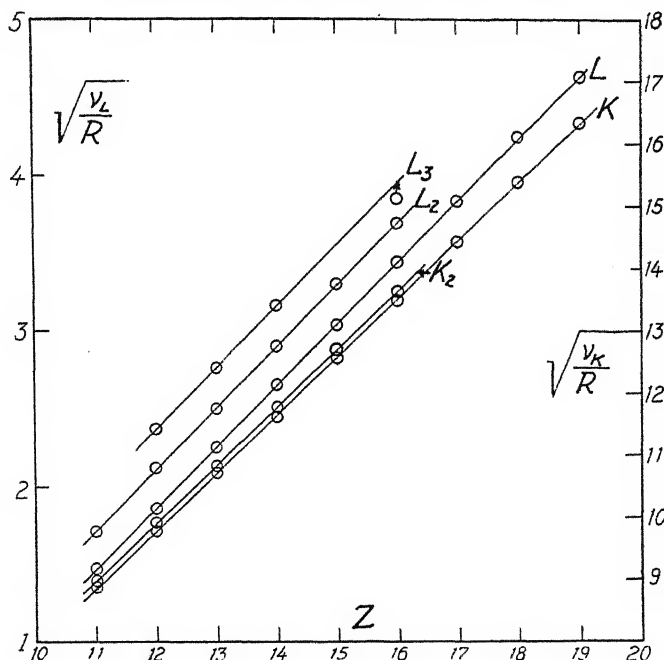


Fig. 1

lines are obtained as shown in Fig. 1. The S point which does not fall on the  $\sqrt{(L)_3}$  line was obtained by use of Hjalmar's measurement of the unseparated  $\alpha_5$  and  $\alpha_6$  lines, which he considered doubtful. The  $(L)_2$  line has an intercept on the  $Z$  axis 0.62 less than that of the  $L$  line, that

being the amount of lessening of the screening constant for the second electron by the removal of the first one. Similarly, the removal of the second one reduces the screening constant for the third one by 0.65 more. Similar parallel straight lines are obtained by plotting values of  $K$  and  $(K)_2$ , also shown in Fig. 1. The removal of the first K electron reduces the screening constant for the second one by 0.16.

After the first K electron has been removed, the second one presumably moves in a circular  $1_1$  orbit around the nucleus. If it were the only electron present the energy necessary for its removal would be  $Z^2$ , in  $\nu/R$  units (neglecting the relativity correction). The presence of the other electrons can have very little effect upon the motion of this electron in its orbit, even though some of the outer electrons probably penetrate within the orbit of this K electron. The times of penetration are such minute fractions of their orbital periods that their effect on the energy of the K electron must be negligible. The energy for the removal of the electron through a cloud of outer electrons fixed in position would be less, however, because of their screening effect and is considerably less in the actual case because of the additional effect of the increased binding of the outer electrons which furnishes more energy. The calculated values of the energies of an electron in a  $1_1$  orbit for the different nuclei, making the relativity correction, are listed in Table III under  $K_2'$ . The difference between  $K_2'$  and  $(K)_2$  gives  $E_2$ . If, as assumed above, the screening of the K electrons is perfect for the outer electrons this decrease in the energy necessary to remove the second electron is the same as the decrease in the energy necessary to remove the first K electron from the atom of next higher atomic number (neglecting the small effect of the added valence electron). That is, the sum of the K term for an atom of atomic number  $Z$  and  $E_2$  for an atom of atomic number  $Z-1$  will give  $K_1'$ , the energy which would be necessary to remove the first K electron if there were no outer electrons present. The calculated values of  $E_2$  and  $K_1'$  are also listed in Table III.  $K_1'$  and  $K_2'$  are thus the energies necessary for the successive removal of two electrons from an ion made up of a nucleus of charge  $Z$  and two electrons, and correspond to the first and second ionizing potentials of helium. Their values give additional data for the testing of theories of the structure of the helium-like ions. There does not seem to be any simple relation between  $K_1'$  and  $K_2'$  for these atoms which will also apply to the two successive ionizing potentials of He.

Hjalmar found one additional K spark line, lying between  $\alpha_1$  and  $\alpha_3$ , which he designated  $\alpha_1'$ . Wentzel suggested that it corresponds to the

transition  $KM \rightarrow LM$ . Applying the same argument as above,  $(KM)_Z = K_Z + M_{Z+1}$  and  $(LM)_Z = L_Z + (M_L)_Z$ .  $(M_L)_Z$ , the energy for the removal of an M electron from an atom which has already had an L electron removed, is unknown. The equation  $(a_1')_Z = (KM)_Z - (LM)_Z$  becomes

$$(a_1')_Z = K_Z + M_{Z+1} - L_Z - (M_L)_Z$$

which reduces to

$$(a_1' - a_1)_Z = M_{Z+1} - (M_L)_Z.$$

The quantity on the left hand side of the equation is positive, so  $M_{Z+1} > (M_L)_Z$ . This means that the removal of an L electron does not increase the energy for the subsequent removal of an M electron as much as the removal of a K electron does. That is, the L electron does not screen the nucleus perfectly, which is quite what would be expected. This last discussion will illustrate the complications which are to be encountered in considering the multiple ionization levels corresponding to the L spark lines which have been observed. Because of the imperfect screening by the L electrons there will be no simple relations between these levels and the ordinary single ionization levels, such as we have found for the levels discussed above.

JEFFERSON PHYSICAL LABORATORY,  
HARVARD UNIVERSITY,  
May 11, 1925.

## RELATIONS OF PP' GROUPS IN ATOMS OF THE SAME ELECTRONIC STRUCTURE

BY I. S. BOWEN AND R. A. MILLIKAN

## ABSTRACT

**Pp' groups of spectral lines.**—(1) *For two-valence-electron atoms.* A quintuplet of nearly equally spaced lines (really an unresolved sextuplet) has now been found for all the two-valence electron spectra which have been studied by the method of hot-spark spectroscopy, namely for the series MgI, AlII, SiIII, PIV, Sv, ClVI, and for BeI, BII, CIII, NIV and Ov. In both of these series, this pp' group has been definitely shown to arise from an electron jump from the lowest  $p$  to the lowest  $s$  orbit, combined with a simultaneous jump of the other electron between the  $p_1, p_2, p_3$  orbits. The frequency differences between groups of successive atoms obey the irregular doublet law, showing that the jumps are between levels of the same total quantum number. (2) *For three-valence-electron atoms.* A new quadruplet pp' group has been discovered for all the atoms of this type studied, AlI, SiII, PIII, SiV, ClV and CII, NIII, OIV. The relative intensity of this group increases with the effective nuclear charge, from AlI to ClV. This group is proved to be due to the return of one of the  $s$  electrons after displacement to a  $p$  position combined with the simultaneous interchange of the  $p$  electron between the  $p_1, p_2$  orbits. This group also obeys the irregular doublet law. These groups are of exceptional theoretical interest because their existence proves that the energy changes due to the simultaneous jumping of two electrons between orbits, are integrated into monochromatic radiation. The mechanism by which such an integration takes place is at present a complete mystery.

**Multiplicity of ionization potentials.**—The ionization potential must depend on the state in which the ionized atom is left after removing an  $s$  electron, for example, and will differ according as the  $p$  electron is left in the  $p_1, p_2, p_3$  or  $P$  orbit.

## 1. HISTORICAL INTRODUCTION

THE so-called pp' group of spectral lines was noticed and carefully compared in the spectra of calcium and strontium by Rydberg<sup>1</sup> in 1894, and a corresponding group was first observed in barium in 1914 by Popow.<sup>2</sup> It was only, however, in 1921 that Götze<sup>3</sup> first interpreted these groups in Ca, Sr, and Ba as corresponding to electronic jumps into the  $p_{1,2,3}$  levels from a group of theretofore unknown triplet levels which he designated as  $p'$  levels. This designation was adopted because a study of the lines missing out of the possible nine combinations between two triplet groups showed that the  $p'$  levels corresponded to the same inner

<sup>1</sup> Rydberg, Wied. Ann. 52, 119 (1894).

<sup>2</sup> Popow, Ann. der Phys. 45, 147 (1914).

<sup>3</sup> Götze, Ann. der Phys. 66, 285 (1921).



quantum numbers as the  $p$  levels, and also because the Zeeman effect observed in these lines corresponded to the predictions of Landé's<sup>4</sup> theory for jumps from one  $p$  level to another.

The exceptional interest of these groups from the standpoint of theory arises from the discovery that when a series of them possessing ordinary spectral series relationships had been found in calcium the term values corresponding to the more remote  $p'$  terms of this series were actually *less than zero*. This is shown by the following numerical values of  $p'$  terms:  $4p' = 10800$ ,  $5p' = 750$ ,  $6p' = -5000$ ,  $7p' = -8300$ , and  $8p' = -10,000$ . The last two of these were worked out by Russell and Saunders.<sup>5</sup> This discovery was made independently by Wentzel<sup>6</sup> and by Saunders and Russell.<sup>7</sup> The negative terms of this series mean that the observed frequency corresponding to a jump from  $6p'$  to  $4p$ , for example, is actually larger than that corresponding to a jump from infinity to  $4p$ . In other words, the observed emitted energy (frequency) is larger than the total energy which the electron has to lose in jumping from infinity to the  $4p$  level. *This additional energy can then only be obtained from the simultaneous jump of some second electron, the total readjustment in energy due to the two jumps being just sufficient to produce the observed frequency.* This suggestion was first made by Bohr.<sup>8</sup>

The significance of this discovery does not lie in the demonstration that the emitted frequency corresponds to the total change in the energy of the atom because of electronic readjustments rather than to the change in energy of some particular electron. For it has long been recognized that the change in position of one electron must of necessity cause a readjustment of the whole electron family within an atom, and also that the emitted radiation must therefore be equivalent to the total energy change. That it is indeed the total energy change in the atom that determines the radiation has been especially clearly demonstrated in the study of band spectra. The significance of the foregoing discovery in the  $pp'$  group lies rather in the proof for the first time brought to light that *two electrons, both of which are in unstable quantum states, may simultaneously perform two definite quantum jumps and integrate these combined jumps into a single monochromatic radiation.*

As to the precise nature of these two jumps this much is definitely known. (1) One of the two jumping electrons, henceforth designated

<sup>4</sup> Landé, Zeits. f. Phys. 5, 231 (1921).

<sup>5</sup> Russell and Saunders, Astrophys. J., 61, 38 (1925).

<sup>6</sup> Wentzel, Phys. Zeits. 24, 106 (1923); 25, 182 (1924).

<sup>7</sup> Saunders and Russell, Phys. Rev. 22, 201 (1923).

<sup>8</sup> Bohr, lecture at Göttingen, 1922. See Phys. Zeits. 24, 106, footnote 1.

as the first, *ends*, or comes to rest, in the lowest vacant  $p$  level, i.e. in the case of calcium in one of the levels  $4p_{1,2,3}$ ; in the case of magnesium in one of the levels  $3p_{1,2,3}$ ; in the case of beryllium in one of the levels  $2p_{1,2,3}$ . This is known because of the 6 lines of the group (these are reduced to 5 in our photographs because with our resolution the two middle ones overlap) certain ones show precisely the separation found in the normal  $p_{1,2,3}$  levels, and these separations occur in such an order as to show that the jump is *to* rather than *from* this group. (2) This same first electron jumps *from* some triplet  $p$  level, as is shown by the relation mentioned in the first paragraph. (3) The other of the two jumping electrons, henceforth designated as the second, *ends*, or comes to rest, in the lowest vacant  $S$  level, i.e.  $4S$  in calcium,  $3S$  in magnesium,  $2S$  in beryllium; for if it did not do so, the normal triplet separation could not appear exactly in a  $pp'$  group, since this normal separation is produced only when this second electron is in the  $4S$  level.

The level *from* which this second electron jumps was thought by Wentzel from his study of calcium to be  $3d$ , since he thought that he found the difference between  $4s$  and  $3d$  of the spark spectrum of calcium to be equal to the amount by which the limit of the  $p'$  terms was different from zero. Russell and Saunders<sup>5</sup> have recently come to the same conclusion. Despite the excellent quantitative agreement found by these observers, the following experimental study of the  $pp'$  group shows that this choice as to the second electron jump cannot be the correct one, *for the cases here studied*, though it may be correct for calcium.

## 2. THE IRREGULAR DOUBLET LAW AND THE $PP'$ GROUP

As is shown in preceding papers, the development of hot-spark spectroscopy has for the first time given us a means of comparing the radiating properties of a long series of light atoms of like electronic structure, such as is constituted by the series of the seven stripped atoms from sodium through chlorine. Letting one electron return to the last six of these atoms gives rise to another series of atoms of like electronic structure which in a previous paper<sup>9</sup> we have called a two-valence-electron series.

Now, previous studies of two-valence-electron systems have revealed a characteristic  $pp'$  group in them all. Thus, this group is found in the arc spectrum of barium, strontium, calcium, magnesium, and beryllium, and in the spark spectrum of aluminum, all of which are two-valence-electron systems. We therefore looked for this group in the spectra of the aforementioned two-valence-electron series and found it at once in the

<sup>9</sup> Bowen and Millikan, Phys. Rev. 25, 591 (May 1925).

spectrum of every element of the series  $Mg_I$ ,  $Al_{II}$ ,  $Si_{III}$ ,  $P_{IV}$ ,  $S_V$ , and  $Cl_{VI}$ , as is shown in Table I.

We then made a similar study of the other two-valence-electron series accessible to our spectroscopic region, viz.,  $Be_I$ ,  $B_{II}$ ,  $C_{III}$ ,  $N_{IV}$ ,  $O_V$ , and found it in every element of this series also, as shown in Table II. How unmistakably this  $pp'$  group stands out on all our plates with its 5 nearly equally-spaced lines, the middle one being always much stronger than the others because it is actually two overlapping lines, may be seen from a glance at Plates I and II.

TABLE I

$pp'$  groups in the two-valence-electron systems,  $Mg_I$  to  $Cl_{VI}$

	$\lambda$ (I.A., vac.)	$\nu$	Diff.
$Mg_I$	2777.503	36003.56	20727.94
	2779.084	35983.08	
	2780.639	35962.96	
	2782.226	35942.44	
	2783.782	35922.35	
$Al_{II}$	1760.12	56814.3	20295.5
	1761.96	56755.0	
	1763.95	56690.9	
	1765.81	56631.2	
	1767.75	56569.1	
$Si_{III}$	1294.52	77248.7	20050.7
	1296.73	77117.1	
	1298.93	76986.4	
	1301.13	76856.3	
	1303.34	76726.0	
$P_{IV}$	1025.58	97506.0	19948.5
	1028.13	97264.2	
	1030.53	97037.1	
	1033.14	96792.4	
	1035.54	96567.9	
$S_V$	849.25	117751.1	19942.6
	852.19	117345.0	
	854.81	116985.6	
	857.83	116573.2	
	860.46	116216.9	
$Cl_{VI}$	724.13	138096.8	
	727.54	137449.5	
	730.31	136928.2	
	733.89	136260.2	
	736.76	135729.4	

The series of differences between the central member of each group, as displayed in column 4, shows how accurately linear is the progression of frequency with atomic number in going down either the series from  $Be_I$  to  $O_V$ , or that from  $Mg_I$  to  $Cl_{VI}$ . This means that *these  $pp'$  groups follow the irregular doublet law*, and this in turn means, as shown in a preceding paper<sup>a</sup> that *the jumps involved must take place between levels of*

the same total quantum number. In the case of the  $\text{Be}_I$  to  $\text{O}_V$  series the jumps in question are definitely limited to jumps between the  $2s$  and  $2p$  levels since there are no other levels of total quantum number 2. This eliminates the possibility of the jump proposed by Wentzel from a  $d$  to an  $s$  level, and with it the selection principle which he invented to make such a jump possible. It eliminates with equal definiteness the theory proposed by Landé<sup>10</sup> that in  $pp'$  groups the second electron always jumps between orbits of different total quantum number. In other words, *the proof is complete and definite that the two electron jumps that combine to give off the  $pp'$  radiations are, in the  $\text{Be}_I$  to  $\text{O}_V$  series, (1) a jump of the first electron between two of the three levels designated as  $2p_1$ ,  $2p_2$ , and  $2p_3$ , and (2) a jump of the second electron from one of the  $2p$  levels to the  $2s$  level.*

TABLE II

*pp' groups in the two-valence-electron systems,  $\text{Be}_I$  to  $\text{O}_V$*

	$\lambda(\text{\AA}, \text{vac.})$	$\nu$	Diff.
$\text{Be}_I$	2651.343	37716.73	23858.8
	2651.438	37715.39	
	2651.507	37714.40	
	2651.585	37713.29	
	2651.652	37712.34	
$\text{B}_{II}$	1623.66	61589.2	23480.8
	1623.86	61581.7	
	1624.08	61573.2	
	1624.25	61567.0	
	1624.46	61558.9	
$\text{C}_{III}$	1174.96	85109.0	23267.2
	1175.31	85084.2	
	1175.72	85054.0	
	1176.03	85031.6	
	1176.40	85005.1	
$\text{N}_{IV}$	922.02	108457.5	23171.2
	922.57	108392.9	
	923.18	108321.2	
	923.68	108262.6	
	924.31	108188.8	
$\text{O}_V$	758.76	131794.0	
	759.52	131662.1	
	760.50	131492.4	
	761.21	131369.8	
	762.18	131202.6	

Since the  $pp'$  group has in all two-valence-electron systems essentially the same structure, it is a natural inference that it always arises from the two jumps just mentioned. If in calcium, for example, the second electron jumps from a  $3d$  to a  $4s$  orbit, as Wentzel and also Russell and Saunders have suggested, then there is here a violation of the selection

<sup>10</sup> Landé, Zeits. f. Phys. 7, 149 (1924).

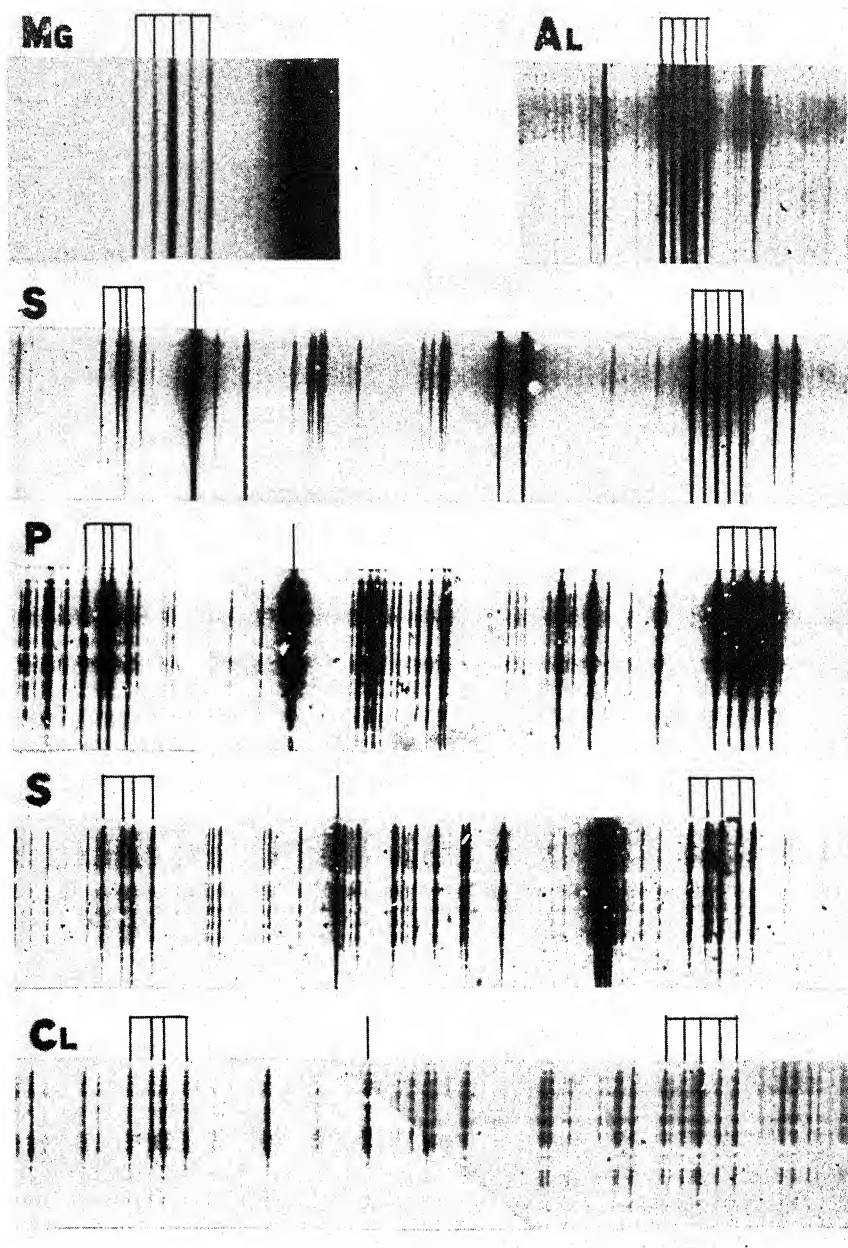


Plate I

principle which has been found to hold for all single electron jumps in the field both of optics and of x-rays, and which the present experiments prove to be valid for two-electron jumps as well, namely, that azimuthal quantum numbers can change only by plus or minus one. This is a difficult assumption to make, and one that is rendered more difficult by the entire absence in calcium of a second  $pp'$  group corresponding to the second electron jump from  $4p$  to  $4s$  such as we have proven to exist in our whole series of two-valence-electron systems. It is certainly to be expected that in calcium too there will be this regular  $pp'$  group in addition to the one attributed by Wentzel to the  $3d$  to  $4s$  jump, but no such second group is found.

TABLE III

*Comparison of frequencies of  $pp'$  group with  $(3S-3P)$  Jump*

	$3S-3P$	$pp'$
MgI	35051.4	35962.96
AlII	59845.1	56690.9
SiIII	82878.9	76986.4
PIV	105190.4	97037.1
Sv	127144.0	116985.6
ClVI	148949.2	136928.2
CaI	23652.4	23254.66
SrI	21698.4	20895.5
BaI	18060.2	10843.5

A partial check upon the foregoing conclusion is obtained as follows: Since the double jump giving rise to this  $pp'$  group always involves the jump from a  $p$  to an  $s$  orbit, and since the second jump which is to be added either positively or negatively to this is quite small on account of the closeness of the  $p_{1,2,3}$  levels to one another it is to be expected that the  $pp'$  frequency will always be nearly the same as that corresponding to the jump from the  $p$  to the  $s$  level, i.e., nearly the same as the frequency of the first term of the principal series. Table III shows that this prediction is verified as closely as could be expected in view of the fact that the jump from the  $P$  to the  $S$  level will, of course, not involve quite the same energy after a nearby electron has shifted its position as before that shift has taken place.

The foregoing conclusion can be verified visually by reference to Plate I, for it states simply that the  $pp'$  group will always appear on any spectral plate close to the first term of the principal series. This is marked upon Plate I, by a single vertical line above it.

In order to permit of a simultaneous two-electron jump of any kind it is necessary that both of the two jumping electrons be at a given instant in a displaced position, i.e., in the particular case under consideration,



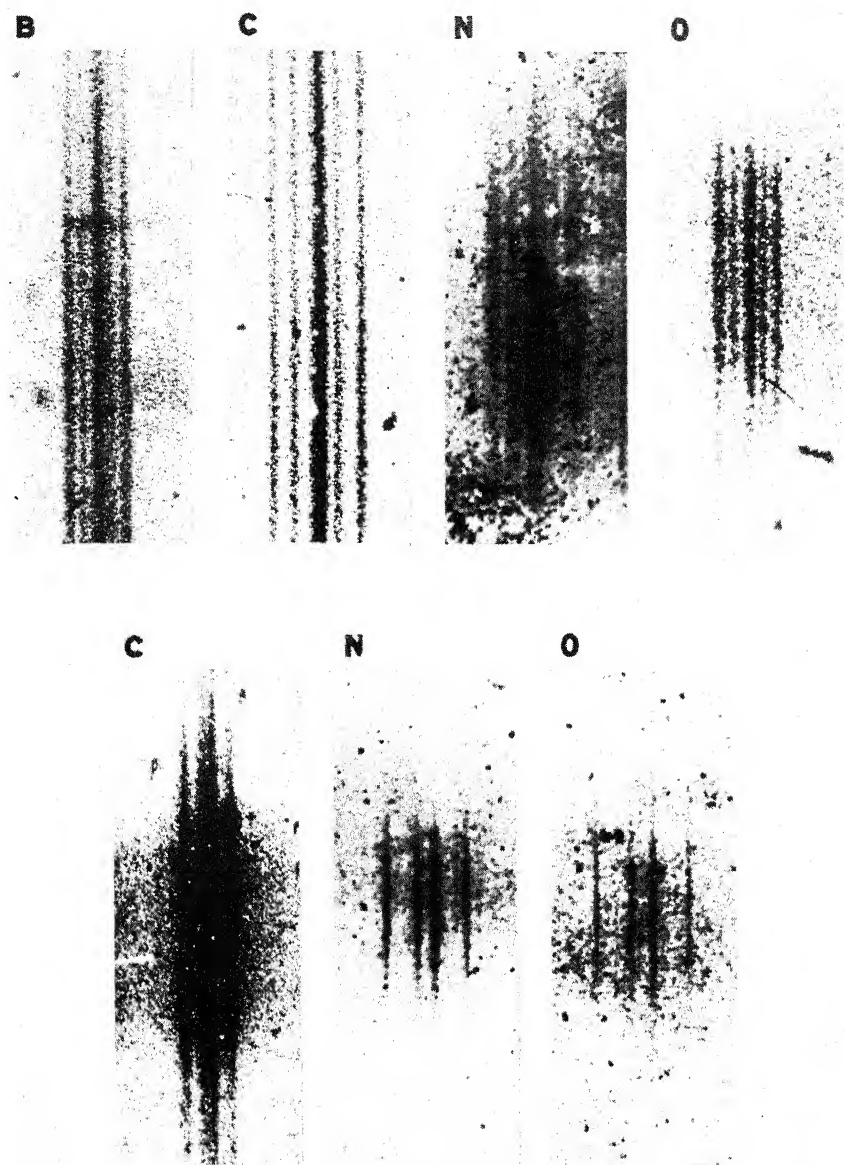


Plate II



that the first electron be in one of the  $2p_{1,2,3}$  levels at the same time that the second electron is in some  $2p$  level. If these two displacements are not the result of a single act, it is necessary that the first electron be held in a metastable position until another act can displace the second electron. The  $2p_1$  and  $2p_3$  levels are indeed metastable, but the  $2p_2$  level is definitely not so. Now the approximate equality in the intensities of the lines of the  $pp'$  groups shows that all three of the levels  $2p_{1,2,3}$  are equally metastable, i. e. equally likely to be the seat of one of the two jumping electrons, when the double jump occurs—a conclusion in accord with the observation, by Green and Peterson,<sup>11</sup> that lines originating in the  $2p_{1,2,3}$  levels are absorbed in equal intensity. We conclude then, that it is one single act that displaces two  $s$  level electrons to the two  $p$  levels, from which they jump simultaneously in the production of the  $pp'$  group.

### 3. PREDICTION OF $PP'$ GROUPS IN THREE-VALENCE-ELECTRON SYSTEMS

Having just shown that when two electrons are found at the same time in the  $p$  levels, they give rise to a  $pp'$  group through the simultaneous jumping of the second of them to an  $s$  level while the first jumps between two of the  $p$  levels, it is pertinent to inquire whether the same sort of phenomenon should not occur whenever in a three-valence-electron system, for example, two of the three valence electrons get at the same time into  $p$  levels; for the situation is then in every respect identical with that discussed in section 2, save for the presence of the third electron in an  $s$  orbit. This last fact ought not to modify in any way the general character of the events to be expected in the return of the two displaced electrons to their normal positions. Thus, the  $pp'$  group for a two-electron system was found when both the electrons were displaced to the  $3p$  level, at least one and probably only one being in the triplet level. Its structure and position showed that one electron returned to the  $3s$  level while the other either remained in its position or else jumped to any other triplet  $p$  level that the selection principle for inner quantum numbers permitted.

In the three-electron system under consideration we have exactly the same situation (two electrons in the  $p$  levels, one of which can return) save for the fact that there is one other electron which remains *all the time* in the  $s$  position and hence modifies by virtue of its field, the energies, or term values of all adjacent positions. We should therefore expect to find here a  $pp'$  group having an energy approximately equal to the difference between that of the  $s$  and  $p$  levels, but since odd-electron sys-

<sup>11</sup> Green and Peterson, *Astrophys. J.* **60**, 301 (1924).

tems always give rise to doublets in place of the triplets characteristic of even-electron systems, the new  $pp'$  group here being predicted ought to be a quadruplet, for this is the structure that would correspond to the four possible combinations between the two  $p'$  levels and the two normal  $p$  levels. The electron which does not return to the  $s$  level can either retain the same inner quantum number or change to the other possible one. In the two-electron system it had the choice of either remaining of the same inner quantum number or changing to a second or third possible one. In the present three-valence-electron case all of the four possible jumps are permitted by the selection principle.

From the foregoing analysis it will be seen that the predicted  $pp'$  quadruplet should reveal in the separation of its components the normal  $p_1p_2$  separation and a second slightly different  $p_1'p_2'$  separation. Further, it is to be expected (1) that this predicted quadruplet  $pp'$  group will be a characteristic of all three-valence-electron atoms, and (2) that since it is produced by a double jump between levels of the same total quantum number, its frequency will progress with atomic number in accordance with the irregular doublet law.

TABLE IV

$pp'$  groups in the three-valence-electron Systems, CII to OIV

	$\lambda$ (I.A., vac.)	$\nu$	Diff.
CII	903.63	110664.8	35203.7
	903.98	110621.9	
	904.17	110598.7	
	904.48	110560.8	
NIII	685.04	145976.9	34533.7
	685.55	145868.4	
	685.86	145802.4	
	686.39	145689.8	
OIV	553.33	180724.0	34533.7
	554.07	180482.6	
	554.52	180336.1	
	555.23	180105.5	

#### 4. THE DISCOVERY OF QUADRUPLT $PP'$ GROUPS

The predictions of the preceding section are verified in every detail by the data presented in Tables IV and V, and by the series of spectrograms shown in Plates I and II. A glance at the plates shows how characteristic of the three-valence-electron system is this quadruplet  $pp'$  group. That it has not been recognized before is due simply to the fact that this group in general falls in the extreme ultraviolet where preceding observers have been unable to do systematic work. Only in the case of

aluminum are the data in Table IV taken from another observer (Paschen<sup>12</sup>) who, however, did not recognize this quadruplet since it was very weak and partially obscured by other strong lines.

TABLE V  
*pp' groups in the three-valence-electron systems, Al<sub>I</sub> to Cl<sub>V</sub>*

	$\lambda$ (I.A., vac.)	$\nu$	Diff.
Al <sub>I</sub>	1762.79	56728.3	27101.8
	obscured		
	1766.31	56615.2	
	1768.95	56530.9	
Si <sub>II</sub>	1190.42	84004.0	25133.9
	1193.31	83800.5	
	1194.50	83717.0	
	1197.42	83512.9	
P <sub>III</sub>	913.99	109410.7	24441.4
	917.14	109035.2	
	918.69	108850.9	
	921.86	108476.0	
S <sub>IV</sub>	744.92	134242.8	24111.2
	748.40	133618.6	
	750.23	133292.3	
	753.76	132668.6	
Cl <sub>V</sub>	629.33	158899.1	
	633.18	157933.0	
	635.31	157403.5	
	639.24	156435.7	

Upon our own plates the  $pp'$  group for Al<sub>I</sub> is too faint to observe. It appears in increasing strength as the nuclear charge increases, as is shown in Table VI. The reason for this is as follows: Since the  $s$  electrons in Al<sub>I</sub> are bound much more tightly than the  $p$  electron, the latter will in general be entirely removed before any of the  $s$  electrons are disturbed.

TABLE VI  
*Increase of intensities of pp' groups with effective nuclear charge*

	Frequency		Intensity	
	$pp'$	$p_2$	$pp'$	$3p-3d$
Al <sub>I</sub>	56615.2	48280.91	2	15
Si <sub>II</sub>	83717.0	131818.	3	7
P <sub>III</sub>	108850.9	243332.1	5	5
S <sub>IV</sub>	133292.3	381541.4	5	6
Cl <sub>V</sub>	157403.5	542000.(est.)	6	4

When, however, the  $p$  electron has been entirely removed the atom has become a two-valence-electron system and hence any jump to an  $s$  level will correspond to a two-valence-electron series and not to the three-valence-electron series. Thus in aluminum the  $p$  electron is gone so much of the time that the characteristic three  $pp'$  electron lines are hard

<sup>12</sup> Paschen, Ann. der Phys. 71, 544 (1923).

to find. With increasing effective nuclear charge the energy required to remove the  $p$  electron continually increases relative to the energy required to lift an  $s$  electron to the  $p$  position, and hence the latter jump becomes more and more frequent.

This follows clearly from the fact that the  $s$  to  $p$  change is an irregular doublet, and hence increases linearly with  $z$ , while the total energy of  $p$  varies as the square of the effective nuclear charge. In Table VI, the last two columns give the relative intensities of the  $pp'$  groups and the strongest lines due to jumps into the  $3p$  level from the  $3d$  level. Column 2 gives the energy necessary to transfer one of the  $s$  electrons to the  $p$  level, while column 3 gives the energy necessary to transfer the  $p$  electron to infinity.

##### 5. SIGNIFICANCE OF $PP'$ GROUP IN THREE-VALENCE-ELECTRON SYSTEM

In a three-valence-electron system it is known from absorption experiments in aluminum vapor, for example, that in the normal state two of the valence electrons are in the  $3s$  level and the third in a  $3p$  level. About

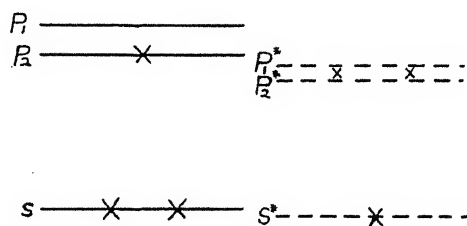


Fig. 1

these three occupied outer orbits (levels) are then arranged the series of virtual orbits in jumping between which the third electron produces the ordinary series of arc lines. This series of orbits is diagrammatically represented by the continuous lines of Fig. 1. When, now, one of the  $3s$  electrons absorbs energy and is thus elevated to a  $3p$  orbit its removal from the  $s$  level changes the field-strength everywhere about the nucleus so that the new series of virtual orbits is now in displaced positions, as represented by the dotted lines. These new orbits are here designated as  $3p_1^*$ ,  $3p_2^*$ , etc.

When, now, one of the two electrons in a  $p$  position jumps back to the vacant  $s$  position the  $3p^*$  levels cease at once to exist, the  $3p_1$ ,  $3p_2$  etc. positions reappearing instantly. Hence, a jump of one electron from a  $3p$  to a  $3s$  position is necessarily accompanied by a shift of the other  $3p$  electrons from a  $3p^*$  level to a  $3p$  level. But when this shift takes place the existence of four lines in the  $pp'$  group shows that the electron which is forced out

of a  $3p^*$  orbit by the jerking of that orbit out from under it, so to speak, may make the shift to a  $3p$  orbit in four different ways: by changing (1) from  $3p_1^*$  to  $3p_1$ , or (2) from  $3p_2^*$  to  $3p_2$  without change in inner quantum number, or (3) from  $3p_1^*$  to  $3p_2$  or (4) from  $3p_2^*$  to  $3p_1$  with change in inner quantum number. The two central lines of the quadruplet  $pp'$  group correspond to the first and second of these changes, the two outer lines to the third and fourth. The fact that the two central lines are not coincident shows that the energy change from  $3p_1^*$  to  $3p_1$  is not quite the same as from  $3p_2^*$  to  $3p_2$ . This is to be expected from the difference in the fields in which the  $p$  and the  $p^*$  orbits lie in virtue of the change of position of an  $s$  electron.

#### 6. MEANING OF IONIZATION POTENTIAL IN MULTIVALENT ATOMS

It is obvious from the foregoing discussion that the  $3s$  term value cannot be obtained by simply adding to the  $3p$  term value in the arc spectrum the frequency of any member of this quadruplet  $pp'$  group. It may be obtained as follows.

Assume that an  $s$  electron is completely removed from the atom. The atom will then be an ionized system with one electron in the  $s$  position and the other in the  $p$  position. The atom can then be brought back to normal by allowing this  $p$  electron to fall into the  $s$  position, thus emitting the first term of the principle series of the spark spectrum. Then if the second electron returns to its normal position it will emit a total energy equal to the term value of the lowest  $p$  orbit of the arc spectrum. But the total energy emitted in restoring the atom must be equal to that necessary to ionize it, i.e. necessary to remove an  $s$  electron. This is at once seen to be for aluminum equal to  $(3s-3p)$  spark spectra plus  $3p$  arc spectra. This is, then, the  $3s$  term value.

The question, however, at once arises as to whether to take one of the triplet  $p$  levels or the singlet  $P$  level in this computation. This forces on us a somewhat more general conception of the meaning of ionization potential as not merely the energy that must be given to an electron to remove it from an atom, but as the total energy given to an atom when a certain one of its electrons is removed. This, of course, will depend upon the state in which the atom is left and hence will be different according as the  $p$  electron is left in the  $p_1$ ,  $p_2$ ,  $p_3$  or  $P$  orbit, so that there may be, and probably are, as many as four ionization potentials for the lowest  $s$  level of these elements, depending upon whether in the readjustment of the position of the  $p$  electron, which follows upon the removal of an  $s$  electron, this  $p$  electron goes in the process of the readjustment into

one or the other of the four levels which are open to it. Measurements of ionization potentials have not yet been made with enough care to test this theory. In thallium, in which the separation of the  $p_1$ ,  $p_2$ ,  $p_3$  levels is relatively large, a measurable difference in ionization potentials might be obtained.

## 7. SUMMARY AND CONCLUSIONS

The fundamental significance of the two electron jumps which are dealt with in this paper lies in the new light which they throw upon the problem of the relation between the energy of ether waves (radiant energy) and atomic or subatomic energy (material energy).

These experiments constitute new proof of the futility of the 19th century attempt to find the origin of monochromatic ether waves in the vibratory motion of charged particles of any sort. Within the past ten years, an atom or molecule has been definitely shown, first by relationships discovered in band spectra, and second by two-electron jumps of the sort herein discussed, to have the capacity of integrating any sort of a complex subatomic or submolecular shudder into a monochromatic ether wave the frequency  $\nu$  of which is determined by  $h\nu = E_1 - E_2$ ,  $E_1$  and  $E_2$  representing the total energy before and after the shudder respectively. The facts of band-spectra show that this integrating process can combine into one emitted frequency a change (1) in the energy of rotation of the two nuclei of a diatomic dumb-bell shaped molecule, (2) in the vibration of these two nuclei along their line of connection, or (3) in the kinetic or potential energy of one of the electronic constituents of the system.

The present experiments along with the studies of Wentzel and of Russell and Saunders, which they supplement, prove conclusively that two electrons may simultaneously change their energies within an atom and integrate their joint energy-change into an emitted monochromatic ether wave. The mechanism by which such an integration takes place is thus far a complete mystery. We are here in the presence of one of the ultimate phenomena of the physical world. The contribution of these experiments to the understanding of this phenomenon consists simple (1) in the proof which they furnish that the particular two-electron jumps which are here integrated are (a) a jump of one electron from a  $p$  to an  $s$  position, and (b) a simultaneous jump of another electron from one  $p$  position to another  $p$  position; (2) in the evidence which they bring to light that every one of a long series of two-valence-electron systems is characterized by essentially the same sort of an easily recognizable

sextuplet  $pp'$  group, this sextuplet appearing without essential modification in such different two-valence-electron systems as  $\text{Be}_I$  to  $\text{O}_V$  and  $\text{Mg}_I$  to  $\text{Cl}_{VI}$ ; (3) in the discovery that a three-valence-electron system is similarly characterized by a quadruplet  $pp'$  group which is found in all the three-valence systems that we have studied; (4) in the proof herein furnished that the variation of the frequency of  $pp'$  groups with atomic number follows the irregular doublet law and hence that the group is formed by jumps between levels of the same total quantum number.

NORMAN BRIDGE LABORATORY OF PHYSICS,  
CALIFORNIA INSTITUTE OF TECHNOLOGY,  
PASADENA.  
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## THE EXCITATION OF FORBIDDEN SPECTRAL LINES\*

BY PAUL D. FOOTE, T. TAKAMINE AND R. L. CHENAULT

## ABSTRACT

Violations of the Bohr selection principles.—(1) A *discussion* indicates (a) that a breakdown of the azimuthal quantum number rule either with or without a simultaneous violation of the inner quantum rule is not infrequent; (b) that forbidden lines may be produced in absorption and otherwise under circumstances which prove the absence of a strong homogeneous electric field. Violations of the inner quantum rule alone are rare; certain of them *may* be produced by a strong magnetic field but those found in the present work were produced in the absence of a strong homogeneous field either electric or magnetic. It is suggested that, possibly, rapidly varying inhomogeneous fields are effective. A careful study of the width of these lines and of the variation of the intensity with density might throw some light on the problem. (2) *1S—2p group in Hg, Cd and Zn.* The forbidden lines  $1S—2p_1$  ( $\Delta j=2$ ) for Hg, Cd and Zn were observed at  $\lambda 2270.0$ ,  $3141.1$  and  $3039.8$  respectively and  $1S—2p_3$  for Cd at  $\lambda 3320.0$  in the positive column of a hot-cathode, low-voltage gradient discharge at low pressure. The intensity of these lines was a maximum at about 250 m-amp/cm<sup>2</sup>, falling rapidly to zero before the current density increased to the point where the sensitive *pd* lines show broadening, an incipient Stark effect produced by the fields of neighboring atoms and ions.

*Cadmium pp' multiplet.*—Four members of this multiplet were photographed in absorption through the positive column against the hydrogen-tube, continuous back ground. It is suggested that the states  $2p_1'$  and  $2p_2'$  may practically coincide.

Spectrograms of mercury series *PD, PS, Ps, ps*, and *pd* are reproduced.

BOHR'S principle of correspondence leads to the formulation of two important laws governing the changes in the azimuthal quantum number  $k$  and Sommerfeld's inner quantum number  $j$  which characterize the quantized states of an atom before and after the emission of a quantum of radiation. The second law may be derived also from the condition of conservation of angular momentum during the radiation process. These two principles of selection will be referred to as Condition  $k$  and Condition  $j$ , and may be expressed by Eqs. (1) and (2) respectively.

$$\Delta k = \pm 1 \quad (\text{Condition } k) \quad (1)$$

$$\Delta j = \pm 1 \text{ or } 0 \quad (\text{Condition } j) \quad (2)$$

subject to the restriction  $(j=0) \nleftrightarrow (j=0)$

The above relations apply to quantized transitions in the complete absence of an external magnetic or electric field. If such fields are present

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many new lines may be expected for which the restrictions in Eqs. (1) and (2) are removed.

#### VIOLATIONS OF THE AZIMUTHAL QUANTUM NUMBER RULE

It appears experimentally established that Condition  $k$  may be broken down by the presence of a strong electric field. Hansen, Takamine and Werner<sup>1</sup> have observed many combinations in mercury up to  $\Delta k = 8$  in their investigation of the Stark effect. The lines for which  $\Delta k = 0$  or 2 were in general the strongest of the "violations," the intensity decreasing for larger values of  $\Delta k$ . Estimates were made of the minimum potential gradient necessary for the excitation of several such lines. For example, the sequence  $2p_2 - mp_1$  ( $\Delta k = 0$ ) appears at field intensities greater than 5000 volts/cm.

If experimental conditions are such that Condition  $k$  is broken down (for the simpler spectra, e.g. doublets and triplets of Groups I, II and III), lines may be excited for which both principles of selection are violated simultaneously. Thus in the above quoted paper we find combinations<sup>2</sup> such as  $2p_1 - 9k$  corresponding to  $\Delta k = 7$  and  $\Delta j$  at least 5 and possibly 6 and 7. The latter figures are not definitely fixed because the triplet  $k$ -terms are unresolved. In general, for the metals of Group II, all combinations with  $2p_1$  involving  $\Delta k \geq 4$  necessitate a simultaneous violation of condition  $j$ ; likewise, all combinations with  $2p_2$  for which  $\Delta k \geq 3$ . That these normally forbidden lines may be excited in the presence of an external field is further supported by numerous scattered observations incidental to the investigation of spark spectra at high potential.

On the other hand, many of the lines so far described appear in the ordinary arc or low-voltage, hot-cathode discharge under conditions where the field intensity due to the applied potential is unquestionably negligible. Foote, Mohler and Meggers<sup>3</sup> employing a discharge tube in which all effects due to the applied field were eliminated by proper screening, observed the doublet  $1s-3d$  of potassium (also sodium) as one of the strongest pairs in the spectrum at 1000 milli-amperes while at 70 milli-amperes its presence was undetected. For the line  $1s-3d_1$  we have  $\Delta k = 2$ ,  $\Delta j = 2$  and for the line  $1s-3d_2$ ,  $\Delta k = 2$ ,  $\Delta j = 1$ . One line therefore violates both selection principles while for the other line Condition  $j$

<sup>1</sup> Hansen, Takamine and Werner, *Det. Kgl. Danske, V. Sel. Math-fys. V*, 3 (1923).

<sup>2</sup> In the present paper we employ Paschen's notation and represent the variable terms by the sequence of letters  $s, p, d, f, g, h, i, j, k, l$  corresponding to the azimuthal quantum numbers 1 to 10 respectively.

<sup>3</sup> Foote, Mohler and Meggers, *Phil. Mag.* **43**, 659 (1922).

is satisfied. These writers suggested that the apparent violations might be attributed to the presence of electric fields due to neighboring ions and electrons. Bohr<sup>4</sup> emphasized this view stating that these local fields, from rough calculation, "may easily have been many thousand times larger than the intensity of the external electric forces present in the unscreened part of the apparatus, as a direct consequence of the applied potential"; that is, of the order of many thousand volts per cm. This explanation is further supported by the quite general enhancement of the forbidden lines in the arc as the current density is increased.

Fukuda<sup>5</sup> lists 85 forbidden lines of mercury appearing in the so-called branched arc; 14 of these are present at a current density of 0.7 amp./cm<sup>2</sup>, while the others are excited in increasing number up to 5.3 amp./cm<sup>2</sup>, the maximum employed.

Unfortunately for the apparently consistent conclusions to which one is led by the above considerations, Datta<sup>6</sup> has observed the lines  $1s-3d$  and  $1s-4d$  of potassium in absorption, using a long column of unexcited vapor. The lines are sharply and completely absorbed as is readily apparent from the beautiful reproductions accompanying his paper. The question of applied fields or of fields due to neighboring ions and electrons is thus eliminated, but one may still assume the existence of fields arising from neighboring atoms. The strong polar character of the alkali atoms, due to the presence of the valence electron on a protruding, eccentric orbit, may very possibly account for a large perturbing field. However, Datta believes that such an explanation is quite insufficient. The lines were observed in absorption at pressures as low as 2.5 mm Hg while the band absorption due to the molecule showed no broadening below 30 mm, a sensitive criterion for the presence of perturbing forces. While the intensity of the forbidden absorption lines increased with pressure, Datta suggests this is due to the larger number of atoms capable of absorbing and that the same effect might be obtained in a very long tube at correspondingly lower pressure.

Recently, Mohler<sup>7</sup> has found the line  $1s-3d$  of potassium to be strongly excited in a low voltage discharge with low current density but comparatively high vapor pressure. The cathode consisted of a nickel sheet 200 cm<sup>2</sup> in area heated to 500°C, from which a total thermionic current

<sup>4</sup> Bohr, *Phil. Mag.* **43**, 1112 (1922).

<sup>5</sup> Fukuda, *Jap. J. Phys.* **3**, 169 (1924); combinations involved are  $PP$ ,  $Pp$ ,  $Pf$ ,  $Pg$ ,  $pf$ , and  $pg$ .

<sup>6</sup> Datta, *Proc. Roy. Soc.* **101**, 539 (1922).

<sup>7</sup> Mohler, *Critical Potentials Associated with Excitation of Alkaline Spark Spectra*, Bureau of Standards Sci. Paper No. 505 (1925).

of 10 milli-amperes was drawn. Potassium was distilled past this surface, condensing above and dropping down. Hence, no estimate can be made of the pressure except that it was variable and occasionally much higher than that ordinarily employed in low voltage arcs. The current density was of the order  $10^{-4}$  amp./cm<sup>2</sup>. The extremely small value of this current suggests that if large interatomic fields are present they are due to neutral atoms rather than to ions.

There is one argument against the presence of large fields. Some of these forbidden lines may be obtained under conditions such that all lines appear very sharp. Large electric fields produce a pronounced broadening of the diffuse series lines, especially for the higher  $md$  terms. This is clearly shown by the reproductions in the paper of Hansen Takamine and Werner. Takamine<sup>8</sup> observed a shift of 2A for the sodium pair  $2p-4d$  in a field of 25,000 volt/cm. If fields attaining this magnitude, as estimated by Bohr, were present in the experiment of Foote, Mohler and Meggers, a decided broadening might have been expected, especially with lines of higher term value in the  $pd$  series. On re-examination of their plates for sodium and potassium we find no indication of broadening.

For the more complex spectra, especially of the elements belonging to the right half of the periodic table, violations of Condition  $k$  of the type described are still less infrequent. In addition, we have numerous primed terms which first appear in the  $pp'$  and  $dd'$  multiplets for metals of Group II, and which increase in complication and number toward the right of the periodic table until in iron, for example, there occur numerous combinations between primed and unprimed terms having the same value of  $k$ . Such combinations are believed to have their origin in the displacement of two electrons at least one of which undergoes interorbital transition during the radiation process. The replacement of the ordinary principle  $\Delta k = \pm 1$  by Laporte's<sup>9</sup> rule  $\Delta k = 0$  may be therefore as consistent physically as it is empirically, since an "inner" electron usually jumps, and certainly Condition  $k$  is not applicable to the inner electrons producing x-ray spectra unless Sommerfeld's azimuthal and the "grund" quantum numbers are interchanged.

In fine, and omitting reference to the primed combinations, existing experiments in which Condition  $k$ , and both Conditions  $k$  and  $j$  simultaneously, are violated indicate that the forbidden lines may be produced in a strong electric field but that a strong homogeneous field is not always the necessary agent. When atomic distances are considered, the

<sup>8</sup> Takamine, *Astrophys. J.* 50, 23 (1919).

<sup>9</sup> Laporte *Zeits. f. Physik* 23, p. 135, 1924.

field due to a single ion attains very large values. For example, at 50 angstrom units from a singly charged ion, the field is 570,000 volts/cm; at 100Å, 143,000, and at 520Å, the average distance between atoms for a pressure of 0.2 mm Hg, the field is 5300 volts/cm. These fields, if homogeneous, should certainly produce in the sensitive lines a Stark broadening. The absence of such an effect, possibly, may be related to the inhomogeneous character of the field. An electron on a circular orbit of diameter 10Å at a distance of 50Å from an ion is in a field which changes from point to point over the orbit with a maximum variation amounting to 170,000 volts/cm. Similar effects of a much smaller magnitude are produced by the field from a neutral atom such as an alkali. It seems, therefore, possible that an inhomogeneous field of this type might introduce harmonics into the motion such that these forbidden transitions may occur quite apart from the disturbances giving rise to an ordinary Stark effect. However, it does not appear likely that this could account for the presence of certain forbidden lines as the most intense lines of the entire spectrum.

Several interesting experiments readily suggest themselves. The width of the diffuse series lines, when the forbidden lines appear, should be investigated with a spectroscope of high resolving power. How narrow are the lines  $1s-3d$  and  $1s-4d$ ? These may be broadened on account of the sensitive  $md$  term. What is the effect of varying the length of the absorbing column in Datta's experiment, keeping the number of absorbing atoms constant? What is the effect of the introduction of helium or argon at high pressure—atoms which should produce but small disturbance on account of their non-polar character? Quantitative measurements on the intensity of  $1s-3d$  for an alkali in a low-voltage, low-current arc at various, controlled vapor pressures are desirable. Probably these lines can be excited below the ionization potential if the pressure is high. What explanation may be offered for the fact that while  $1s-3d$  may be the most intense line in the potassium spectrum, apparently it has been so far impossible to excite many other combinations, for example the series  $1s-ms$ ?

#### VIOLATIONS OF THE INNER QUANTUM RULE

Exceptions to the selection principle for inner quantum numbers, alone, are extremely rare. In spite of the numerous lines in multiplet spectra for which  $\Delta k=0$  no violation of Condition  $j$  has been recorded. Paschen and Back<sup>10</sup> (the second Paschen-Back effect) showed that the

<sup>10</sup> Paschen and Back, *Physica* 1, 261 (1921).

rule could be broken down by a magnetic but not by an electric field. Working with fields up to 40,000 gauss they were able to excite the *complete*  $pd$  triplets of Ca, Zn and Cd and the *complete*  $pd$  doublets of Al and  $\text{Ca}^+$ . The line  $p_3d_1$  corresponds to  $\Delta j=3$  and the lines  $p_3d_2$ ,  $p_2d_1$ , of the triplet and  $p_2d_1$  of the doublet involve  $\Delta j=2$ .

Hansen, Takamine and Werner observed  $1S-2p_1$  ( $\Delta j=2$ ) of Hg in a condensed discharge, but after several experiments with magnetic fields up to 19,000 gauss and electric fields up to 35,000 volts/cm they conclude that the excitation of the line cannot be attributed to either a *homogeneous* magnetic or electric field. It is suggested that the line is produced by the perturbing action of the forces from neighboring atoms and ions, constituting a rapidly changing and very inhomogeneous field.

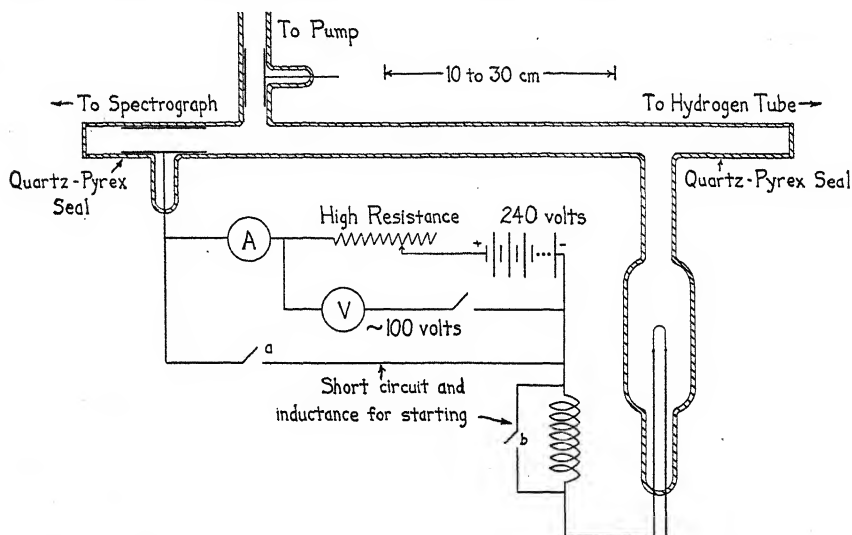


Fig. 1. Discharge tube. This was maintained at a suitable temperature by a surrounding furnace. In starting, the procedure is (1) open  $b$  (2) momentarily close  $a$ . After arc starts  $b$  may be closed.

Takamine and Fukuda<sup>11</sup> observed the line in the branched arc. Its intensity, under the most favorable conditions, was stronger than  $2p_2-9d_2$  but fainter than  $2p_2-8d_2$ , lines lying in the same spectral region. If the current density was either increased or decreased from this optimum condition the relative intensity of the forbidden line diminished.

After confirming the work of Takamine and Fukuda, the present writers employed a simple two-electrode tube of the form illustrated in Fig. 1. The entire tube was heated to a temperature such that the line

<sup>11</sup> Takamine and Fukuda, Phys. Rev. 25, 23 (1925).



$1S-2p_2$  barely showed absorption against an under-water spark or hydrogen tube as background, with no potential on the main discharge tube. The metals investigated were Hg, Cd and Zn, and under the above conditions  $1S-2P$  (except Hg where the line is inaccessible) showed complete absorption extending over several angstroms. Probably the pressure was of the order of several tenth-millimeters. The positive column of the glow was photographed end-on with a Hilger E2 spectrograph. Quartz windows had been sealed to the tube by means of intermediary glasses. The potential drop between the hot tungsten or coated platinum cathode and ring anode was of the order 100 volts, but the discharge tubes were of such length, 30 to 100 cm, that the voltage drop per mean free path of the electrons was very small. The spectrum was strictly of the arc type; only a few of the readily excited spark lines such as  $1s-2p$  appeared, and these in comparatively low intensity. Exposures were made with the ring anode, both in the line of sight and in a short side tube, but the spectra obtained were identical. No spectroscopic effect of the inductance at  $b$  was observed. Table I gives the observed forbidden lines which are reproduced in Plate I, A, B, C.

TABLE I  
 $1S-2p$

Element	Notation	$\lambda(\text{air})$ observed	$\lambda(\text{air})$ computed	Density visually estimated
Hg	$1S-2p_1$	2270.0	2269.80	(a) 0.5
	$1S-2p_2$	2536	2536.52	5.
	$1S-2p_3$	?	2655.58	...
Cd	$1S-2p_1$	3141.1	3141.16	(b) 0.4
	$1S-2p_2$	3261	3261.04	4.
	$1S-2p_3$	3320.0	3319.85	0.3
Zn	$1S-2p_1$	3039.8	3039.82	(c) 0.2
	$1S-2p_2$	3075	3075.88	2.
	$1S-2p_3$	?	3094.26	...

(a) Intensity lies between  $m=8$  and  $9$  of series  $2p_2-md_2$ .

(b) Intensity = 4 relative to  $\lambda 3082.7$  ( $2p_2-3S$ ) as 10, visually estimated.

(c) Intensity = 1 relative to  $\lambda 3035.93$  ( $2p_2-2s$ ) as 20, visually estimated.

Hg  $1S-2p_3$ , if faintly present, would have been obscured by the strong arc line  $\lambda 2655.13$  ( $2p_2-4D$ ). Zn  $1S-2p_3$ , if faintly present, would have been obscured by band structure. Had it been excited in the same intensity as  $1S-2p_1$ , however, its presence should have been detected.

The above intensities apply for the most favorable current density of about .250 amp./cm<sup>2</sup>. Increase or decrease of the current around this optimum value markedly diminished the intensity of these lines relative to other series lines in their neighborhood. Forbidden lines of the type



observed by Fukuda at very much higher currents were absent, and in the few cases where the resolving power was sufficient to show the complete  $pd$  triplets, no evidence for the presence (by abnormal intensity of superposed components) of forbidden members could be detected. The forbidden lines listed entirely vanish when the current density is increased to the point where the sensitive  $pd$  lines show broadening. This is astonishing inasmuch as broadening is the most sensitive indication known for the perturbing action of interatomic fields. Re-examination of plates made several years ago in this laboratory by the method employed for the excitation of  $1s-3d$  of K shows Cd  $1S-2p_1$  faintly developed at 10 volts and 400 milliamperes.

In summary, while experiment shows that the inner quantum number rule may be broken in the presence of a large homogeneous magnetic field with certain combinations, with others a homogeneous field is insufficient. Violations which cannot be produced in a strong field occur where no applied field is present and under conditions such that other indications, e.g., broadening, point to the absence of a field.

Bohr and Sommerfeld have both shown by an application of the principle of correspondence that a magnetic and not an electric field should be effective in breaking down the selection principle for inner quantum numbers. Paschen and Back's experiments are quite widely quoted as proof that the field must be comparable to the interatomic field which gives rise to the ordinary complex structure. The complete triplets, for example, are excited when the applied field gives a Zeeman separation about equal to the normal separations of the triplet  $d$ -levels. Hence, a homogeneous field of  $10^8$  gauss should be necessary to produce the line  $1S-2p_1$  of Hg. Even local or inhomogeneous fields of this magnitude are totally impossible in a discharge tube. The field due to a Bohr magneton along its axis and at the average distance apart of the atoms at 0.2 mm pressure is only  $10^{-4}$  gauss. Therefore, if the forbidden lines appearing in Plate I are produced by a magnetic field, the field must be weak and inhomogeneous, and the phenomenon is quite different from that observed by Paschen and Back. At any rate, it is satisfying to note that, contrary to examples discussed for the break down of the azimuthal quantum number rules, the intensities of the forbidden lines listed in Table I are relatively weak. Thus assuming a gamma value of unity for the plate characteristic, the ratio of intensities of the allowed and forbidden lines is  $10^5$  with an error of possibly the factor 10. This great difference is not clearly apparent in Plate I, since contrast has been suppressed in the reproduction.

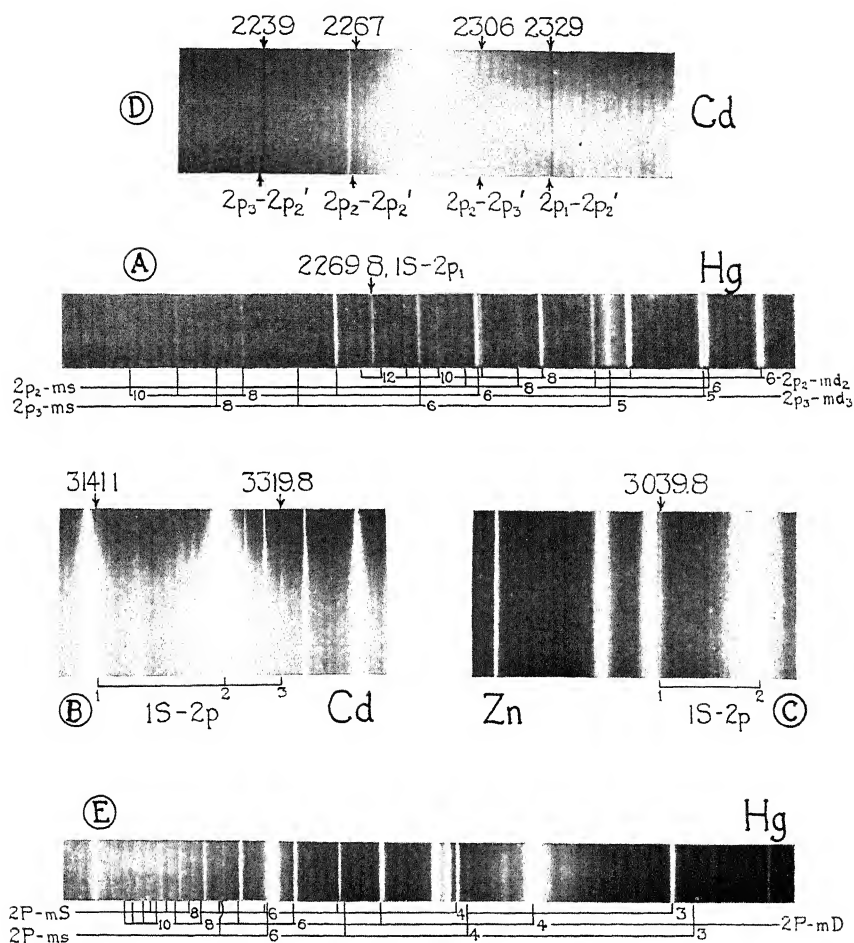


Plate I. (A) Hg  $1S-2p_1$ ; (B) Cd  $1S-2p_{1,3}$ ; (C) Zn  $1S-2p_1$ ; (D) Cd  $pp'$  multiplet in absorption; (E) strong development of Hg  $PD, PS$  and  $PS$  series in positive column.

It should be emphasized that while the results quoted raise no objection to either of the selection principles in their general applicability, consideration of the rapidly increasing number of forbidden lines cannot be dismissed with the single comment that their excitation is due to electric and magnetic fields. The subject is involved and requires investigation of the effect of rapidly varying fields, from both the theoretical and experimental standpoint.

#### CADMIUM $pp'$ MULTIPLET

Compton, Turner and McCurdy<sup>12</sup> have shown that the positive column contains a high concentration of excited atoms. All subordinate series lines are therefore absorbed, but the emission is so strong that the absorption is not readily apparent against a bright background; special photometric computations are usually required for its detection. However, in cadmium an interesting group of emission lines are known which, according to Ruark and Chenault,<sup>13</sup> belong to a  $pp'$  multiplet. This should consist of six members but the two lines involving the  $2p_1'$  term are missing although from intensity rules they should be strong. The known group of four is reversed in the arc and three of the lines have been observed reversed in the under-water spark.<sup>14</sup> In emission the intensities of these lines are weak compared to subordinate series lines; hence with a high concentration of atoms in the  $2p$  states, absorption against the continuous spectrum of the tungsten under-water spark or hydrogen tube should be readily detected as shown in Plate I, D. Table II gives the wave-lengths and classifications.

TABLE II  
*Cd pp' multiplet*

Notation	$\lambda_{air}$ (obs.)	Kayser (Vol. 7)
$2p_3-2p_2'$	2240.0A	2239.86 RS 6
$2p_2-2p_2'$	2267.4	2267.47 RS 4
$2p_2-2p_3'$	2306.7	2306.63 R 4
$2p_1-2p_2'$	2330.0	2329.9 RS 8

*R*=reversed in arc; *S*=reversed in under-water spark

The failure to find the lines involving  $2p_1'$  in emission suggests that transitions from this *initial* state are improbable. Our failure to detect them in absorption, although the region from  $\lambda 2400$  to  $2150$  was carefully investigated, indicates that transitions to the *final* state  $2p_1'$  are improbable. Dr. Laporte and the writers have considered the alternative

<sup>12</sup> Compton, Turner and McCurdy, Phys. Rev. 24, 597 (1924).

<sup>13</sup> Ruark and Chenault, J.O.S.A. and R.S.I. 10, 653 (1925).

<sup>14</sup> Strücklen, Zeits. f. Physik 30, 24 (1924).

that the  $2p_1'$  and  $2p_2'$  terms are practically coincident. Such an assumption makes the intensity relations somewhat better and requires that the lines  $\lambda 2267$  and  $\lambda 2330$  be unresolved doublets.

Certain of the lines are occasionally absent in absorption and some of them appear in emission against the continuous background. A systematic correlation of these phenomena would be quite involved. Table III gives several examples selected from three typical plates. The last exposure listed is the one reproduced in Plate I, D.

In addition to the  $pp'$  absorption group, a weak, sharp absorption line was found at  $\lambda 3086.7$ . This line is not given in any table nor is its classification known.

TABLE III  
*Cd  $pp'$  multiplet in emission and absorption.*

Plate	Exp. No.	Volts	Current	$\lambda 2240$	$\lambda 2267$	$\lambda 2306$	$\lambda 2330$
113	2	110	1000ma.	<i>Eh</i>	<i>Avf</i>	<i>A</i>	<i>Eh</i>
	4	105	400	<i>A</i>	<i>A</i>	<i>A</i>	<i>A</i>
	5	120	105	<i>A</i>	<i>A</i>	<i>A</i>	<i>A</i>
114	1	150+	80	<i>A</i>	<i>Avf</i>	Absent	<i>A</i>
	2	115	275	<i>A</i>	Absent	<i>Evf</i>	<i>A</i>
	3	75	50	Absent	Absent	<i>E</i>	Absent
	4	40	150	Absent	Absent	<i>E</i>	<i>Ef</i>
116	1	100	300	<i>A</i>	<i>A</i>	<i>A</i>	<i>A</i>

*A* = Absorption; *h* = hazy;  
*E* = Emission; *f* = faint; *vf* = very faint.

Of passing interest is the reproduction Plate I, E, showing strong development of the *PD*, *PS* and *Ps* series of Hg. This was made with a wide slit and a current density of about 20 m-amp./cm<sup>2</sup> at 100 volts. Apparently the positive column viewed end-on is very good for the investigation of the series terms of higher order.

FEBRUARY 16, 1925,  
BUREAU OF STANDARDS,  
WASHINGTON, D. C.

LINE BREADTHS AND ABSORPTION PROBABILITIES  
IN SODIUM VAPORBY GEORGE R. HARRISON<sup>1</sup> AND J. C. SLATER

## ABSTRACT

Molecular broadening of the absorption lines of the principal series of sodium.—From recently published experimental data the theoretical half-breadths of the lines 2 to 8 are calculated, together with the half-breadths in frequency units ( $P/2\pi$ ), which are proportional to the probabilities. The broadening of the first line is at least 100 times as great as that to be expected from Stark effect and collision broadening and the breadths of succeeding lines are found to decrease rapidly with increasing term number at the saturated vapor pressures used (450 to 600°C), a result contrary to that commonly found at low vapor pressures. It is suggested that this high pressure broadening is due to the presence of a large proportion of diatomic sodium molecules in varying states of stability which disturb the absorbing atoms far more than an inert gas would, the perturbation being greater the lower the quantum state. As evidence for this the *absolute values of the probabilities  $A_{ij}$  and  $B_{ij}$*  come out only about one fiftieth as large as would be expected if all the gas was in the atomic condition; moreover, the bands associated with line 3303 have about 50 times the total intensity of the line. Incidentally, the half-breadth is found to vary approximately as the square root of the number of absorbing atoms.

Molecular aggregation in saturated sodium vapor at high temperatures.—The above results indicate that the proportion of diatomic molecules increases with the temperature, possibly greatly exceeding the proportion of atoms at 600°C. This suggests that the *energy of dissociation of  $\text{Na}_2$*  at absolute zero may be negative.

## INTRODUCTION

IN a paper recently published by one of the writers<sup>2</sup> the results of an experimental investigation of the shapes and intensities of absorption lines in the principal series of sodium were given, and from these were calculated the relative probabilities of the various transitions involved, by means of formulas derived by the other writer<sup>3</sup> on the basis of his theory of virtual oscillators. The relative probabilities  $B_{ij}$  were obtained for the second to sixteenth lines, and from these were calculated the relative probabilities  $A_{ij}$  by means of Einstein's relation,  $A_{ij} = (8\pi h\nu_0^3/C^3)B_{ij}$ .

In the present paper are given the half-breadths of the second to eighth lines at various vapor densities, and from these are computed the corresponding values of the probability  $P/2\pi$ , which controls line breadths.

<sup>1</sup> National Research Fellow.

<sup>2</sup> Harrison, Phys. Rev. 25, 768 (June 1925).

<sup>3</sup> Slater, Phys. Rev. 25, 783 (June 1925).

Approximate determinations of the absolute values of  $A_{ij}$  and  $B_{ij}$  are also given, and the apparent necessity of assuming the presence of large numbers of diatomic molecules of varying grades of stability in saturated sodium vapor at temperatures over  $400^\circ\text{C}$  is discussed. The notation in this paper is the same as in the preceding papers.<sup>2,3</sup>

#### DETERMINATION OF LINE BREADTHS

It has become the custom to specify the amount of broadening of an absorption line in terms of its half-breadth, or breadth at the point where the amount of absorption is one-half that at the maximum. Theoretically,

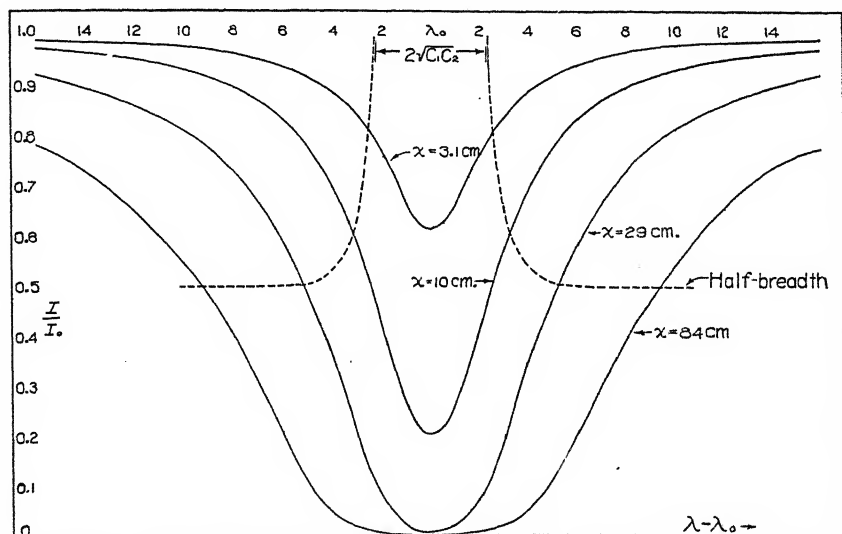


Fig. 1. Curves showing the change in shape of an absorption line with length of the absorbing column. The dotted line shows the changing value of apparent half-breadth with length of column, although the true half-breadth, given by the fundamental value  $2\sqrt{C_1C_2}$ , remains constant.

the full breadth of a single line is infinite, and the absorption is still very appreciable at a point where the breadth is three times the half-breadth, when the broadening is produced by collisions, Stark effect, or other effect giving the broadening formula used in the present work. The shape of a line changes with the distance it has traveled through the absorbing medium, and although each point on the curve obeys the exponential law, its area, and consequently the amount of absorption, does not. This is illustrated in Fig. 1, which shows the changing shape of a line with length of absorbing column  $x$  as computed from the formula  $\log_{10}(I/I_0) = -C_1/[(\lambda - \lambda_0)^2 + C_1C_2]$ , where

$$C_1 = (NB_{ij}hP\lambda_0^3 \cdot 10^{-8}/2\pi^2c^2 \log_e 10)x \text{ and } C_1C_2 = [P\lambda_0^2/2\pi c 10^8]^2.$$

The half-breadth of a line with which we are concerned in finding  $P/2\pi$  is the fundamental value given by  $2\sqrt{C_1C_2}$  and is that for an infinitesimal layer of absorbing medium; the half-breadth measured directly on the photographic plate, on the other hand, is given by a more complex formula and is of small importance, varying tremendously, as the figure shows, with the value of  $x$  used. The values of  $C_1$  and  $C_2$  were taken from experimental data for the value  $x=10$  cm, and the product  $C_1C_2$  was kept constant while  $C_1$  was varied in the other curves to show the effect, on a given line, of using vapor columns of different length but the same vapor density. From these curves it appears that the best condition for measuring  $C_1$  and  $C_2$  accurately is a short column of vapor for the lower members of the series, and a long column for the higher members, such as was used by Wood and Fortrat<sup>4</sup> in extending the sodium principal series to 58 members.

Values of  $C_1$  and  $C_2$  were found for each line, as in the previous paper,<sup>2</sup> and from these were calculated the true half-breadths in angstroms from the formula  $\Delta=2\sqrt{C_1C_2}$ , and also the probabilities  $P/2\pi$ , where  $P/2\pi$  is the half-breadth in frequency units divided by two. In Table I is given a typical set of values of  $C_1$  and  $C_2$  and the corresponding values of half-breadth and probability.

TABLE I

*Line breadths*

Vapor pressure 18 mm

Plate 25B4						
Line	Wave-length	$C_1$	$C_2$	$\sqrt{C_1C_2}$	Half-breadth	$P/2\pi$
2	3303A	17.90	1.1	4.43	8.86A	$12.1 \times 10^{11}$
3	2853	2.45	1.2	1.71	3.42	6.3
4	2680	.95	1.3	1.11	2.22	4.65
5	2594	.42	1.5	.794	1.58	3.54
6	2543	.22	1.8	.629	1.25	2.91
7	2512	.153	2.1	.567	1.13	2.70
8	2491	.129	2.4	.557	1.11	2.69
9	2475	.107	2.8	.548	1.09	2.70

In the calculation of  $A_{ij}$  and  $B_{ij}$  from the measured constants it was possible to average the relative values for all vapor densities and thus get very accurate values by taking the mean of eighteen determinations, once it had been found that the relative probabilities were not a function of vapor density. In this way  $N$ , the relative number of absorbing atoms in each case, was found with apparently considerable accuracy. In the case of  $P/2\pi$ , which depends on  $N$ , this was not possible, since the product of  $C_1$  and  $C_2$  is involved, whereas in the preceding case their

<sup>4</sup> Wood and Fortrat, *Astrophys. Jour.* **43**, 73 (1916).



ratios were averaged and the curve smoothed out. In Fig. 2 the half-breadths of three lines are plotted against the relative numbers of atoms absorbing them, the latter being determined, as in the previous paper, from the calculations of  $B_{ij}$ . Although the points do not lie very exactly on smooth curves, the general nature of the relation between  $\Delta$  and  $N$  is fairly evident, since it seems logical to assume that the curves all pass through the origin. For line 3303 ( $n=2$ ) the curve has the form  $\Delta = kN^{.53}$ ; for line 2853 ( $n=3$ ) the equation is  $\Delta = k'N^{.54}$ ; and for line 2680 ( $n=4$ )  $\Delta = k''N^{.51}$ . Whether or not the apparent variation of the exponent with wave-length is real, the similar values of the exponents obtained for the three lines would indicate that  $\Delta$  may be expected to vary, for a

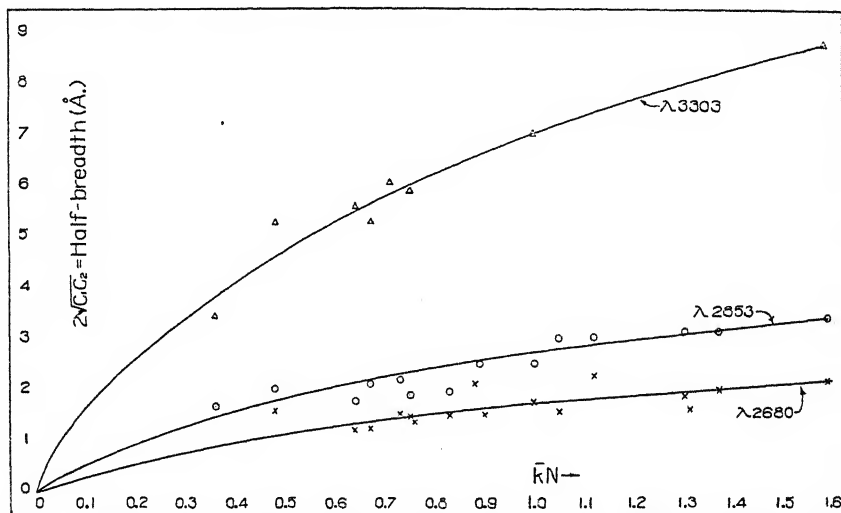


Fig. 2. Curves showing the relation of fundamental half-breadth of lines 2, 3 and 4 to number of absorbing atoms.  $K$  is a proportionality constant. The curves are approximately simple parabolas in the region studied, and although they undoubtedly pass through the origin, should not be as drawn at low vapor pressures because of the relatively increased importance of Stark effect or broadening due to collisions of the second kind.

given line, with a power of  $N$  close to one-half, if not this exactly. While it is true that both coordinates in these curves were calculated from  $C_1$  and  $C_2$  as determined in the present experiments, one depends on their ratio and the other on their product. Thus one would not expect experimental errors to be masked.

In Table II are given the values of  $P/2\pi$  determined for lines 2 to 7 at selected vapor densities. Where several values were obtained at almost the same density they were averaged by means of curves similar

to those given in Fig. 2. The half-breadths of the lines in angstroms can be found from the values obtained by means of the formulas given above. Although values of  $P/2\pi$  for lines up to the sixteenth were obtained, no great confidence is felt in the accuracy of those above the eighth, because of the difficulty of determining exactly the resolving power of the

TABLE II  
*Line breadth and vapor density*

$kN$	$P/2\pi \times 10^{-11}$ for lines 2 to 7					
	2	3	4	5	6	7
.48	6.4	3.9	3.3	3.1	2.8	2.4
.67	7.3	4.0	2.9	2.9	2.8	2.6
.73	8.2	4.2	3.3	2.9	2.6	2.3
.88	9.1	4.8	3.5	3.6	3.2	2.8
1.00	9.6	5.1	3.8	3.3	2.8	2.6
1.37	11.3	5.9	4.2	3.8	3.5	3.1
1.59	12.1	6.3	4.6	3.5	2.9	2.7

spectrograph used. If this was greater than the value assumed, it would change the half-breadths measured for the higher members considerably, but would not greatly affect those before the eighth line, beyond making the  $P/2\pi$  vs  $n$  curve slightly steeper. An error of this sort would not alter greatly the  $A_{ij}$  and  $B_{ij}$  values given in the previous paper.

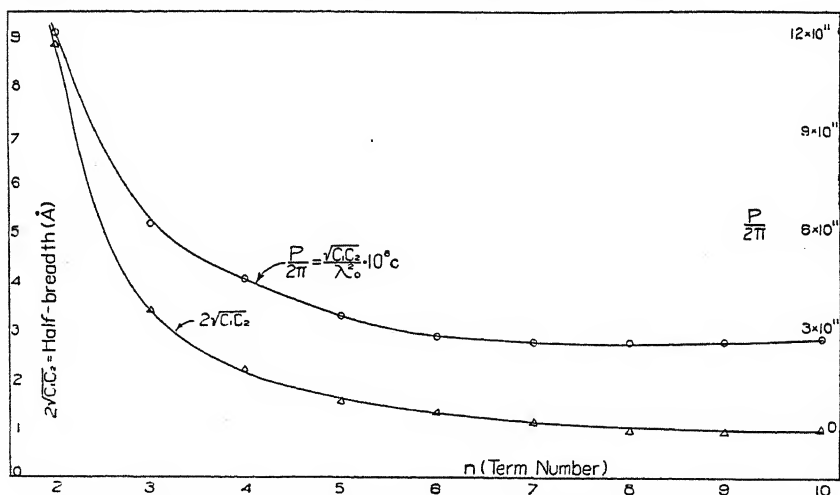


Fig. 3. Curves showing the variation of half-breadth, both in wave-length and frequency units, with term number, for the second to tenth lines of the sodium principal series absorbed by saturated vapor at 590°C.

In Fig. 3 are shown values of the half-breadth in angstroms, and also of  $P/2\pi$ , plotted against term number for a given vapor density. Curves similar to these were plotted at a number of vapor densities; some were

found to exhibit a more pronounced rise in  $P/2\pi$  after the sixth term, increasing steadily out to the sixteenth. This may be a spurious effect resulting from incorrect estimate of resolving power, or a real phenomenon due to Stark effect or collision broadening.

#### DISCUSSION OF THE CAUSE OF LINE BROADENING

A most important result is the fact that the half-breadths of lines in the principal series of sodium, and presumably in all the alkali metals, decrease as the term number increases, for the first few members, at least, at the vapor pressures used. This is at variance with experimental results at low pressures and with theoretical attempts to explain the broadening on the basis of collisions or Stark effect. The magnitude of the breadth for the first few lines is extraordinarily great in comparison with the breadth at low pressures. Füchtbauer and Schell,<sup>5</sup> for example, give a value for  $P/2\pi$  of only  $1.73 \times 10^{11}$  for the D-lines at a temperature of  $174^\circ \text{C}$ , with a pressure of 1733 mm of nitrogen. They found that the broadening varied directly with the pressure of foreign gas, so that at 30 mm this would give a value of  $P/2\pi = 3 \times 10^9$ . We find for the second line of the series  $P/2\pi = 1.2 \times 10^{12}$  at a pressure of not over 30 mm and a temperature of  $590^\circ \text{C}$ , or 400 times the computed broadening. This is a minimum value, since in our experiments the D-lines were undoubtedly broader than line 3303. The explanation of this difference would seem to be that the present large broadening is bound up with the fact that the pressure here is largely the vapor pressure of sodium itself at high temperature, while in the other experiments the pressure was produced by a foreign gas. This would imply that neighboring sodium atoms or molecules possess a capacity of disturbing other sodium atoms very much greater than that possessed by other kinds of molecules, except possibly those of other alkali metals. This is discussed later.

It should be pointed out that the very great broadening of the lower series lines obtained in this work is not unique, but is apparent in all published photographs of alkali vapor absorption where high vapor pressures were used and where much band absorption was present. Wood's photographs<sup>6</sup> of sodium absorption show a rapid decrease in breadth with increasing term number, as do those of Datta<sup>7</sup> for potassium vapor. While certain photographic phenomena might combine to create a false appearance of decreasing breadth in particular cases, careful

<sup>5</sup> Füchtbauer and Schell, *Phys. Zeits.* **14**, 1164 (1913). See also Füchtbauer and Hoffmann, *Ann. der Phys.* **43**, 96 (1914).

<sup>6</sup> Wood, *Phil. Mag.* **18**, 530 (1909).

<sup>7</sup> Datta, *Proc. Roy. Soc.* **101**, 539 (1922).

study shows that this cannot explain away the effect in all, and in the present work, of course, such possibilities are definitely ruled out. At low vapor pressures, on the other hand, it is frequently observed that the breadth of series lines increases rapidly with term number.

The band spectrum of sodium consists of a number of groups or systems, one apparently associated with each of the first few lines of the principal series, rapidly decreasing both in intensity and extent as we go up the series. This strongly suggests that corresponding to each principal series level of the atom there is a system of molecular energy levels, the band about a line arising when the electron in the molecule makes the same transition that the electron in the atom would make for the line. In a situation where dissociation is taking place the molecules are not all in one definite state, but there are a variety of possible states for them, varying from strongly bound molecules to half-formed ones which persist only a short time, and finally to mere pairs of mutually disturbing atoms. The last would form band energy levels only slightly displaced from the atomic energy levels, and a great many such would coalesce to produce the effect of a broadened atomic level. The absorption spectrum would then consist of bands about the lines, with broadened lines about the frequencies of pure atomic transitions. Assuming this to be the cause of the observed broadening we can connect the empirical fact that the bands become much less conspicuous about higher lines of the series with the decrease in broadening in passing up the series. The interpretation of the decrease in intensity in bands is not obvious, but if the bands are due to stable molecules, the broadening to unstable ones, it seems reasonable to suppose that the same factors that affect the magnitude of the bands should also affect the amount of broadening.

An interesting observation in connection with this possible explanation of the present broadening is furnished by the analogous cases of potassium, rubidium, and caesium. There the lines show distinct satellites<sup>8</sup> which seem to be of molecular origin. It may well be that these satellites represent very loosely bound molecules, and that the situation in sodium is similar, but that the satellites, instead of being separate lines, are distributed in such a way as to produce simply a broadened line of regular form.

The necessary condition, both for the large broadening and its decrease with increasing term number, thus becomes the presence of a sufficient number of molecules to produce the broadening, which will be indicated

<sup>8</sup> See Datta *loc. cit.*,<sup>7</sup> and rubidium and caesium absorption photographs by Bevan, *Proc. Roy. Soc.* **83**, 421 (1910) and **85**, 54 (1912).

by the associated band absorption. There may then be three causes of broadening: that connected with bands, that due to Stark effect, and that due to collisions of the second kind, the two latter causes predominating at low vapor pressures, and the first at high vapor pressures.

Holtmark<sup>9</sup> has treated the observed broadening at low vapor pressures on the basis of the Stark effect from the electric field of neighboring atoms, and one of the authors<sup>10</sup> has suggested a broadening on account of the collisions of the second kind. It seems likely that in a more complete development of quantum theory than we have at present, these two effects will appear as related. Neither is at all capable of explaining the present phenomena observed at high vapor pressures. The Stark effect seems to indicate broadening of the order of that observed by others when the pressure arises from a foreign gas, but there is no apparent reason why a greatly increased action should arise when the external gas is sodium. The effect of collisions of the second kind seems small in the present case; it would be important only if atoms could produce such collisions when they approached within distances of the order of  $10^{-6}$  cm from atoms in the second or third quantum states.

The decrease of breadth with term number is also difficult to interpret on the basis of Stark effect or collision broadening. For the excited states connected with the principal series transitions are states where the valence electron is in a long, eccentric orbit, the length increasing rapidly with term number. The Stark effect would increase with term number, for it depends on the amount of time the electron is out of the intense field of the inner part of the atom and is comparatively free to be influenced by the external field, and this increases rapidly with the longer orbits. Collisions of the second kind might naturally be supposed to increase with term number, the larger orbits being easier to hit than the small ones. These explanations then suggest increase of breadth with term number, which is observed only at low vapor pressures. If we suppose that both these effects and the molecular broadening are operating, however, all the experimental facts are explained.<sup>11</sup>

It should be pointed out that in the previous paper<sup>2</sup> the constants  $C_1$  and  $C_2$  were determined on the basis of a formula for line shapes which

<sup>9</sup> Holtmark, *Ann. der Phys.* **58**, 577 (1919).

<sup>10</sup> Slater, *Phys. Rev.* **25**, 396 (1925).

<sup>11</sup> Since the above was written, a paper by Born and Franck, *Zeits. f. Phys.* **31**, 411 (1925) has appeared, in which the authors suggest the existence of unstable or quasi-molecules in a dissociating gas. Their idea is that the broadened bands around absorption lines may be connected with such molecules. Their point of view is similar to that suggested in the present paper.

was found to hold experimentally. Such shapes would be given by Stark effect or collisions of the second kind, but no assumption need be made as to the exact cause of broadening.

#### ABSOLUTE ABSORPTION PROBABILITIES

In the formula for the probabilities of transition from the  $i$  state to the  $j$  state with the absorption of radiation,  $B_{ij} = (3.31 \times 10^{37} / N x \lambda_0) \sqrt{C_1 / C_2}$ , we can assign absolute experimental values to every factor except  $N$ , the number of absorbing atoms, from data already given. To determine  $N$ , however, involves the determination of the vapor densities in each case, and, since saturated vapor was always used, of the temperature. In previous similar investigations of line absorption coefficients the experiments have been made at low vapor pressures, only the first few members of the series being studied, and it was possible to enclose the absorbing vapor in a glass or quartz vessel which furnished a definite boundary to the absorbing column. Also the temperature could be determined accurately, the vapor being kept under uniform conditions for long periods of time. In the work here discussed this was not possible, since sodium vapor at the temperatures desired attacks all known substances transparent to ultraviolet light, and it was necessary to use the dynamic equilibrium method common in qualitative studies of alkali vapor absorption, the hot vapor being enclosed in a steel tube provided with water jackets which cooled the ends and condensed the vapor before it reached the windows. The molten pool of sodium in the center of the tube was thus continually providing vapor for distillation into the ends, the rate of distillation being made slow by small-apertured stops at the ends of the hot portion of the tube, and by the presence of a few centimeters pressure of hydrogen. In order to get even an approximate value of the pressure it is necessary to have recourse to indirect methods.

The *relative* number of absorbing atoms in each of the eighteen vapor densities studied was obtained with a fair degree of accuracy in the manner indicated in the previous paper.<sup>2</sup> A fair absolute approximation for  $N$  in any given case could thus be made by assigning upper and lower limits to the temperature, determining the corresponding vapor pressures, and balancing the 4.42-fold range of densities between them. It should be emphasized that the relative values of  $N$  can be determined with an accuracy entirely independent of the error in the absolute values.

Ladenburg and Minkowski<sup>12</sup> have summarized the available data on the vapor pressure-temperature curve of sodium, and from their curve

<sup>12</sup> Ladenburg and Minkowski, *Zeits. f. Phys.* 6, 153 (1921).

and the relative values of  $N$  obtained from absorption measurements in this work the approximate vapor densities were computed. The highest pressures used were not over 30 mm, as measured on a mercury manometer, the cold hydrogen in the manometer and the hot hydrogen and hot sodium in the furnace being practically in mechanical equilibrium. Ladenburg and Minkowski<sup>12</sup> state that in their experiments on the D-lines, the red and yellow absorption bands appeared in a short vapor column at temperatures near 400°C, which checks with previous measurements made on Na vapor by one of the writers. At the lowest density used in this work for which reliable relative values of  $N$  were obtained, the bands around the D-lines were very strong, completely wiping out the lines, while the second set of bands around line 3303 was beginning to appear. It was possible, however, to get approximate measurements for a few lines under conditions close to those used by Ladenburg and Minkowski, and by using their data on the vapor pressure-temperature curve, and their observations on the temperature at which the first bands appeared, the probable range in our experiments was set at 4 mm to 18 mm of sodium vapor pressure. We will proceed to calculate  $N$  on this basis, and from it  $B_{ij}$  and  $A_{ij}$ . Using the gas law, we have for the number of molecules per cm<sup>3</sup>,  $N = 2.71 \times 10^{19} (273/T^0) p / 760$ . We will assume the vapor to be monatomic, as is usually done, although forced to amend this view later, and taking the case of line 3303 at the highest vapor density, we have  $T = 863^\circ\text{K.}$ , and  $p = 18$  mm, so  $N = 2.02 \times 10^{17}$ . Then since  $C_1 = 17.9$  and  $C_2 = 1.1$ , we have  $B_{ij} = 3.31 \times 10^{37} \times 4.04 / 2.02 \times 10^{17} \times 10 \times 3303 = 2 \times 10^{16}$ . Also  $A_{ij} = (5.45 \times 10^{36} / N \pi \lambda_0^4) \sqrt{C_1/C_2} = 0.9 \times 10^5$ . This value is for the second line, and the curve connecting  $A_{ij}$  and term number was rising so steeply at this point that it was impossible to extrapolate to the D-lines with any accuracy. We may take 30, the value of  $(A_{ij})_{5893} / (A_{ij})_{3303}$  computed by Ladenburg from Bevan's data, as a maximum value; we then obtain roughly  $(A_{ij})_{5893} = 3 \times 10^6$ . If we assume that the a priori probability is proportional to the number of energy levels into which the term is split up in a magnetic field, this would make  $A_{ij}$  one-third as great. In general, lines of this sort are found to have an  $A_{ij}$  of the order of  $10^8$ . Line 2537 of Hg vapor, on which much work has been done, has a probability of about one-tenth this value, but this is explained on the basis that it is a combination line. We may suppose, therefore, that the value of  $A_{ij}$  computed above is perhaps one hundredth of the value to be expected.

On going over the details of the computation and the assumptions made, we find that  $A_{ij}$  can be increased by making  $N$  or  $\pi$  smaller, or by



making  $C_2$  relatively smaller to  $C_1$ . The main purpose of the previous investigation<sup>2</sup> was to determine the last two factors, and our arguments rest on the assumption that the values obtained for them are substantially correct. The fact that the relative values of  $B_{ij}$  were found to be independent of  $N$  is taken to indicate that no large error was made. The length of the absorbing column  $x$  was uniformly 10 cm, which was the distance between the stops in the furnace. The column might have been slightly greater in length at higher vapor densities, but it could not have been less, as required to increase  $A_{ij}$ .

$N$  could be made less if we assume the temperature to have been taken too high, but a number of things make this highly improbable, and at best it could only account for a factor of about two. The chief cause of the discrepancy may well be the presence of molecular aggregates, which were neglected in the above computation and which would give a new value of  $N$ , only a fraction of the molecules being monatomic and contributing to the line absorption. In order to make  $A_{ij}$  attain the theoretical value, we should have to assume the presence of from ten to 100 times as many molecules as atoms, with the most probable figure around fifty. That this is not an extravagant assumption we will endeavor to show below.

#### THE EVIDENCE FOR MOLECULAR AGGREGATES

Vapor density determinations in the alkali metals are extremely difficult, and have generally been carried out at much lower temperatures than those used here. There is considerable disagreement between the results of different observers, especially at high temperatures, when different methods were used. The presence of band absorption can be taken as quite certain indication of aggregates of atoms into molecules, and Smith<sup>13</sup> has recently analyzed some of the visible bands in Na and finds moments of inertia which seem to indicate the presence of  $\text{Na}_2$ . We accordingly have here a further justification in assuming the presence of a certain number of  $\text{Na}_2$  molecules in the present case, although at temperatures below  $400^\circ\text{C}$ , where the vapor pressure is about 0.3 mm, the number of molecules is undoubtedly smaller than the number of Na atoms. The effect of rising temperature is to increase dissociation, but where the vapor is saturated, as in this work, the pressure rises faster than the temperature, tending to reverse the effect.

If we were to apply conventional thermodynamics, we should have the equilibrium constant, or the ratio of the square of atomic concentra-

<sup>13</sup> Smith, Proc. Roy. Soc. 106, 400 (1924).

tion to molecular concentration, equal to  $aT / pe^{-q_0/RT}$ , where  $a$  is a constant,  $\beta$  equals  $3/2$  if the specific heat of the molecules is  $(5/2)R$ , and  $q_0$  is the energy required to dissociate a molecule at absolute zero. With increasing  $T$  and  $p$ , the factor  $T^\beta$  increases, as does also  $e^{-q_0/RT}$ , if  $q_0$  is positive, but  $p$ , the vapor pressure, increases so rapidly that the whole quantity would decrease, for reasonable choice of constants, meaning an association into molecules. It sometimes happens, however, that  $q_0$  is negative, in which case we find that the formula permits even so large a change as from practically all atoms at  $400^\circ\text{C}$  to mostly molecules at  $600^\circ\text{C}$ . Also, if there are many partly formed molecules, these would have energy in their internal degrees of freedom, and hence the specific heat of the molecules would be greater than  $(5/2)R$ , and  $\beta$  would be reduced. While some exception might be taken to the use of the above formula in the present case, it seems to be true that such formulas work better than would be expected from the assumptions made in their derivation. It is interesting to note that the chemical constants of sodium and potassium, as determined by Ladenburg and Minkowski,<sup>14</sup> show discrepancies from the theoretical values larger than for any other monatomic vapor, giving the impression that they may depart appreciably from being monatomic even in the region where measurements have been made on them with presumably accurate results.

Approximate photometric measurements on the bands associated with line 3303 indicate about fifty times as much total intensity of band absorption as of line absorption at  $600^\circ\text{C}$ . Then, even if we assume all the absorption in the broadened line to have been due to atoms, if the molecular and atomic absorption coefficients are of the same order of magnitude we have definite indication of many more fairly stable molecules than of atoms. There seems few data available to test the justification of such an assumption.

Finally, the intensity of band absorption was measured at various vapor pressures, and a function of this which should be proportional to the number of absorbing molecules was plotted against the previously determined relative numbers of atoms absorbing at the corresponding vapor pressures, the latter being plotted as abscissas. These curves showed a gradually increasing slope as the vapor pressure increased, indicating that the number of molecules was increasing faster than the number of atoms.

We may conclude, then, that the presence of bands indicates with certainty that the alkali metal vapors are not entirely monatomic when

<sup>14</sup> Ladenburg and Minkowski, *Zeits. f. Phys.* **8**, 137 (1921).

saturated above 400°C, and that there is good evidence from the relative changes in band and line absorption that the number of molecules increases faster than the number of atoms with increasing temperature. If we assume the molecular absorption coefficient to be of the same order of magnitude as that of the atom, there must be more molecules than atoms at 600°C. In case there are many more molecules than atoms at high temperatures, the low values for  $A_{ij}$  found in the present work are explained; that the spectroscopic data on which these values are based are trustworthy is indicated by the fact that the ratios of the  $A_{ij}$ 's are found independent of  $N$ . Although it seems a rather forced assumption, and we make it only tentatively, it seems worth considering.

We wish to acknowledge the kindness of Professor E. C. Kemble in giving this paper the benefit of his criticism.

JEFFERSON PHYSICAL LABORATORY,  
HARVARD UNIVERSITY,  
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## THE ABSORPTION SPECTRUM OF LEAD VAPOR IN THE ULTRAVIOLET

BY R. V. ZUMSTEIN

## ABSTRACT

**Absorption spectrum of lead vapor, 5000 to 2000Å.**—Using a column of vapor about 3 cm long in a carbon tube at various temperatures up to 1600°C, absorption was found at 34 lead lines, of which 20 are new. The results may be interpreted very well on the basis of the energy diagram given by Thorsen and Grotrian. Absorptions were observed only from the normal state  $2p_4$  and the metastable states  $2p_3$  and  $2p_2$ . The introduction of the  $2p_5$  state does not seem to be necessary. Additional combinations have been found with the terms  $X_1$  and  $X_2$ . A new term  $X_3$  (10232) is proposed. Values are suggested for the terms  $3p_2$ ,  $3p_3$ ,  $4p_2$ ,  $4p_3$ . Evidence is given for interchanging the terms  $3d_1$  and  $3d_2$  and for a new series ( $2p_3-mx$ ).

**Arc spectrum of lead.**—The spectrum of a 100-ampere Pb arc was photographed to 2000Å and three new lines measured. The line 2070Å may be due to silver and 2189Å seems certainly to be due to lead and not to bismuth.

THE previously described method<sup>1</sup> of obtaining the absorption spectra of metallic vapors has been used for lead.

The absorption spectrum of lead vapor was first studied by McLennan and Zumstein.<sup>2</sup> With an absorption cell, 6 cm long and heated to 750°C, they obtained absorption at the wave-lengths 2833, 2170, 2053.8, 2022.6. Grotrian<sup>3</sup> has recently used an absorbing column of lead vapor 30 cm long and heated to 1200°C. He found fifteen absorption lines of wave-length greater than 2400Å. On the basis of the lead series found by Thorsen<sup>4</sup> and his own absorption experiments, Grotrian was able to give a classification of the lines which appears to be a great advance in our knowledge of the lead spectrum. The terms  $2p_1$ ,  $2p_2$ ,  $2p_3$  and  $2p_5$  correspond to metastable states. The normal state of the lead atom corresponds to the term  $2p_4$ .

A very important verification of the Thorsen-Grotrian scheme has been found by McLennan, Young and McLay.<sup>5</sup> They have obtained the arc spectrum of lead in the Schumann region and get strong reversals in the series ( $2p_4-ms$ ) and ( $2p_4-md_1$ ). The present experiments were under-

<sup>1</sup> Zumstein, Phys. Rev. **25**, 523, (1925).

<sup>2</sup> McLennan and Zumstein, Trans. Roy. Soc. Canada, Sec. III, 9, (1920).

<sup>3</sup> W. Grotrian, Zeits. f. Phys. **18**, 169 (1923).

<sup>4</sup> Thorsen, Die Naturwissenschaften **11**, 78, (1923).

<sup>5</sup> McLennan, Young and McLay, Trans. Roy. Soc. Can. Sec. III, 77 (1924).

taken to extend Grotrian's work to shorter wave-lengths and also to become more familiar with the type of absorption spectra produced by this method. As in the previous experiments,<sup>1</sup> the absorbing vapor was in a carbon tube with open ends and heated with an oxy-acetylene flame. The wave-lengths at which absorption was observed are given in Table I. The series notation given for each line is based on the Thorsen-Grotrian classification.

TABLE I  
*Lead absorption lines observed*

$\lambda$ (I.A.)	Series notation	$\lambda$ (I.A.)	Series notation
4057.826	$2p_2-2s$	2401.943*	$2p_3-X_1$
3683.471	$2p_3-2x$	2399.598*	$2p_3-4d_2$
3639.583	$2p_3-2s$	2393.802*	$2p_3-X_3$
2873.324	$2p_2-3d_3$	2388.809*	$2p_2-4d_1$
2833.071	$2p_4-2s$	2332.423*	$2p_2-4s$
2823.199	$2p_2-3d_2$	2253.94*	$2p_2-5d_3$
2802.009	$2p_2-3d_1$	2246.891*	$2p_3-4d_2$
2663.173	$2p_2-X_2$	2237.427*	$2p_3-4d_1$
2657.105*	$2p_3-3d_3$	2218.08*	$2p_2-5s$
2628.293*	$2p_2-3s$	2189.606*	$2p_3-4x$
2614.200	$2p_3-3d_2'$	2187.89*	$2p_3-4s$
2613.678	$2p_3-3d_2$	2170.00	$2p_4-3d_2$
2577.278	$2p_2-X_1$	2135.46*	$2p_2-7d_1$
2476.390*	$2p_3-X_3$	2115.04*	$2p_3-5d_2$
2446.196	$2p_3-3s$	2111.76*	$2p_3-5d_1$
2443.840	$2p_3-3x$	2088.2*	$2p_3-5x$
2411.742*	$2p_2-4d_3$	2087.4*	$2p_3-5s$

\* New absorption lines.

The absorption at 2833 and 2170 appeared at low temperature (about 700°C) and became very broad at the highest temperature (1600°C). At 2399.6 and 2388.8 the absorption was very faint. The absorption at 2614 and 2613 became somewhat diffuse at high temperatures, all the other absorption lines being sharp and easily recognizable. As lead impurities, absorption was found at the copper pair 3247, 3274 and the bismuth lines 3067, 2231.3, 2228.6 also at the tin line 2246 and at 2311.7 which could not be identified.

A comparison of these results with Grotrian's paper shows in general a confirmation of the series scheme which he gives. The  $X_1$  term 10371 which was calculated from one line  $2p_2-X_1$  has been supported by the combinations  $2p_1-X_1$ ,  $2p_3-X_1$ ,  $2p_4-X_1$ . This explains the absorption of  $\lambda 2022$  ( $2p_4-X_1$ ) at low temperatures. The  $X_2$  term 11,622 calculated by Grotrian from  $2p_2-X_2$ , also combines with  $2p_3$  and  $2p_1$ . The wave-lengths of these combination lines are given in Table III.

The absorptions at 3262 and 3240, reported by Grotrian, come from  $2p_1$ . In the present experiments no trace of absorption was found at

these two wave-lengths nor at any others which originate from the  $2p_1$  state. It would appear that Grottrian used a spectroscope of larger dispersion or that he confused the copper pair (3247, 3274) with the lead lines 3262 and 3240. The dispersion of the spectroscope in these experiments was 6Å per mm at  $\lambda 3200$ .

Considering these results from the point of view of Saha's theory of temperature excitation, it may be stated that with a column of lead vapor at  $1600^\circ\text{C}$  and about 3 cm long, we get absorptions from the normal state  $2p_1$  and from the excited states  $2p_3$  and  $2p_2$ , where  $2p_4 - 2p_2 = 10653$ , and  $2p_4 - 2p_3 = 7821$ , but not from the  $2p_1$  state, where  $2p_4 - 2p_1 = 21464$ . These results are apparently in agreement with those of Sur and Ghosh<sup>6</sup> on the absorption of potassium vapor at  $1200^\circ\text{C}$ . They obtained absorption at the subordinate series. This would require potassium atoms in an excited state differing in frequency from the normal state by  $13000/\text{cm}$ . It may be possible to make a detailed, experimental study of Saha's formula in the laboratory with lead vapor, this being an element where the excited states can be obtained at temperatures within the limit of laboratory methods. Lead has moreover a decided advantage over the alkali vapors as its vapor is much more inert chemically.

It was surprisingly easy to keep the temperature of the carbon tube at an intermediate value (about  $1200^\circ\text{C}$ ) such that while very clear absorptions were shown at lines coming from the  $2p_3$  state, there were no traces of absorptions from the  $2p_2$  state. The frequency difference between  $2p_3$  and  $2p_2$  is only  $2832/\text{cm}$ .

The  $2p_5$  term was introduced by Grottrian to account for the absorption at the line 3684 ( $2p_5 - 2s$ ). This term enters into so few combinations that a classification is here proposed which does not require the  $2p_5$  term. Plates which were taken at an intermediate temperature and which showed absorptions from  $2p_3$  but not from  $2p_2$ , indicated very clearly absorptions at the following unclassified lines: 3684, 2444, 2394, 2189, 2088.2 and at no others. It is therefore clear that these lines originate from a state very near  $2p_3$ . Since the first absorption line 3684 is close to 3640 which is the first line of the sharp series ( $2p_3 - ms$ ), it might be expected that if some of these absorption lines formed a new series, the members would be very close to the sharp series. That this is true is shown by Table II.

A reference to Rydberg's Interpolation Table shows that these lines do have approximately the separations of a series. Using the last two lines of the series and the same table, the limit of the series is found to be

<sup>6</sup> Sur and Ghosh, Phil. Mag. p. 60 (Jan. 1925).

52008. It is therefore assumed that the series originates from the  $2p_3$  state.

Of the 34 lead lines which have been observed in the present absorption experiments, all originate from the levels  $2p_4$ ,  $2p_3$  and  $2p_2$ . The only unclassified line is 2394. Since this line is observed on plates which show absorption lines from  $2p_3$  but not from  $2p_2$  and also is not absorbed by the vapor at low temperatures, we may conclude that it comes from the

TABLE II

*New lead series ( $2p_3=51992$ )*

Values of $m$ :	2	3	4	5
Sharp series ( $2p_3-ms$ ):	3639	2446	2187	2087.4
New series ( $2p_3-mx$ ):	3684	2444	2189	2088.2

state  $2p_3$ . It therefore allows us to calculate a new term  $X_3$  ( $X_3=10232$ ).

Following up this point of view we see that the frequency difference 327, which was noticed by Saunders<sup>7</sup> and by Meissner<sup>8</sup> occurs between the states  $2s$  and  $2x$ . This frequency difference was given by Meissner for two pairs of infrared lines and for two pairs of visible lines. From these

TABLE III

*New lead combination lines*

$\lambda$ (I.A.)	$\nu$ (I. vac.)	Series notation
3572.741	27981.9	$2p_1-X_1$
2401.943	41620.3	$2p_3-X_1$
2021.96	49440.8	$2p_4-X_1$
3739.947	26730.7	$2p_1-X_2$
2476.390	40369.3	$2p_3-X_2$
2393.812	41760.2	$2p_3-X_3$
3683.474	27140.6	$2p_3-2x$
2443.85	40906.6	$2p_3-3x$
2189.61	45655.8	$2p_3-4x$
2088.2	47881.	$2p_3-5x$
10650.8	9386.40	$2s-3p_2(?)$
10291.3	9714.30	$2x-3p_2(?)$
13101.9	7630.45	$2s-3p_3(?)$
12563.8	7957.21	$2x-3p_3(?)$
6011.76	16629.5	$2s-4p_2(?)$
5895.68	16956.9	$2x-4p_2(?)$
6235.317	16032.3	$2s-4p_3(?)$
6110.57	16360.6	$2x-4p_3(?)$
2170.00	46068.5	$2p_4-3d_1(?)$

four pairs we calculate four more terms:  $3p_2=15138$ ,  $3p_3=16894$ ,  $4p_2=7895$ ,  $4p_3=8492$ . The only reason for calling these terms  $3p_2$ ,  $3p_3$ , etc. is that with  $2p_2$  and  $2p_3$  they form a sequence having approximately the same term values as those given by Paschen and Gotze<sup>9</sup> for the  $mp$

<sup>7</sup> Saunders, *Astrophys. J.* **43**, 240 (1916).

<sup>8</sup> Meissner, *Ann. der Phys.* **71**, 135 (1923).

<sup>9</sup> Paschen and Gotze, *Seriengesetze*, p. 144.



terms of the spectra of other elements. The values of  $3p_2$ ,  $3p_3$ ,  $4p_2$  and  $4p_3$  must therefore be accepted with reservation until more evidence is available.

In the Schumann region, McLennan, Young and McLay<sup>5</sup> find that  $2p_4$  combines with all the  $md_1$  terms but the first and also with the first  $md_2$  term but none of the higher  $md_2$  terms. It is therefore possible that we should assign 2170 to the position  $2p_4 - 3d_1$  and not  $2p_4 - 3d_2$  as given by Grotrian. This would involve interchanging the terms  $3d_1$  and  $3d_2$  in Thorsen's series. In Table III are given the new combinations. Those which are considered doubtful are followed by a question mark.

The various term values are collected in Table IV.

TABLE IV  
*Terms in lead series*

Term	$\nu$	Term	$\nu$	Term	$\nu$
$X_2$	10232	$4p_2$	7895	$2x$	24851
$3p_2$	15138	$4p_3$	8492	$3x$	11085
$3p_3$	16894	$3d_1$	13742	$4x$	6336
				$5x$	4111

#### EXPERIMENTS WITH A 100-AMPERE ARC

In connection with these absorption experiments, the lead arc in air has been examined. The lower terminal was a carbon rod, 3 cm in diameter, with a 2 cm hole drilled out of the center and filled with lead. The upper terminal was a 1 cm carbon with the tip about 3 mm from the lead surface. With currents of 100 amperes there was a very intense arc between the upper carbon and the molten lead. This arc was steady and did not exhibit the customary habit of such heavy arcs to wander. The spectrum from this arc was examined with a quartz spectroscope having a dispersion of 4A per mm in the region of 2100. The line given by McLennan, Young and McLay<sup>5</sup> at 2070.05, intensity 1, was not observed. It may be due to silver. They give a list of twenty-three other lines between 2020A and 2255A of which twelve were reversed in a heavy arc. In a 100-ampere arc all of these twenty-three lines were reversed, on an intense continuous background. The line given by them as 2088.4, intensity 5R, appeared as a triplet of wave-lengths 2088.2, 2087.4, 2086.8. A reversal was also observed at 2110.6 and another of considerable intensity at 2242.6.

The line 2189.6 which is of about the same wave-length as a strong bismuth line is not usually attributed to lead. I have compared the spectrum of lead with that of bismuth, using these heavy arcs. On plates which gave the lead spectrum without any trace of the characteristic

bismuth pair 2228.6 and 2231.3, the line 2189.6 was of its customary intensity. This is evidence that 2189.6 is a lead line and its position in the series is given as  $2p_3 - 4x$ .

NATIONAL RESEARCH FELLOWSHIP,  
PHYSICS DEPARTMENT,  
UNIVERSITY OF MICHIGAN.  
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## PHOTO-ELECTRIC IONIZATION OF CAESIUM VAPOR\*

BY PAUL D. FOOTE AND F. L. MOHLER

## ABSTRACT

**Measurement of photo-electric ionization in gases.**—The current from a filament, normally limited by space charge, is increased by the presence of positive ions. As shown by Kingdon this effect may be greatly magnified if a small cathode is practically enclosed by the anode so that the ions are imprisoned. This method was used for the detection of photo-electric ionization. Besides possessing extreme sensitivity it is unaffected by photo-electric emission from the electrodes.

**Photo-electric effect in caesium vapor.**—The change in thermionic current with the unresolved radiation from a mercury arc was measured as functions of the applied voltage, filament temperature, and vapor pressure. Then the photo-electric effect as a function of wave-length was studied using a monochromatic illuminator to disperse light from the arc or a Mazda lamp. The ionization per unit flux was found to increase with increasing wave-length to a sharp maximum at the limit  $1s = 3184\text{\AA}$  of the principal series, as is required by the Bohr theory. For longer wave-lengths the ionization decreased to about 10 percent at  $3400\text{\AA}$ . *Photo-excitation.* The simple theory does not admit of ionization by wave-lengths greater than  $3184\text{\AA}$  but the data are in qualitative agreement with the hypothesis that such radiation produces excited atoms which upon collision with other atoms acquire sufficient additional energy to become ionized. Hence, unlike an x-ray limit, the photo-ionization effect for a valence electron is not sharply discontinuous at the true threshold for direct ionization.

**Photo-ionization photometer and intensitometer.** A tube of the type described, with suitable gases for the range of wave-length involved, may be used as a photometer or may be calibrated to measure intensity of radiation directly.

## HISTORICAL SUMMARY

THE status of the subject of the photo-electric effect in vapors, up to 1922, was summarized in Chapter X of the *Origin of Spectra*.<sup>1</sup> Here it was pointed out that while all direct experiments had failed to demonstrate the existence of the phenomenon, its presence was indicated by the continuous absorption, exhibited by a monatomic vapor, of frequencies greater than that corresponding to the highest term in the arc spectrum.

Since then much more satisfactory evidence for the continuous absorption has been obtained by Harrison<sup>2</sup> who has made quantitative measure-

\* Published by permission of the Director of the Bureau of Standards, Department of Commerce.

<sup>1</sup> Foote and Mohler, *Origin of Spectra* Chemical Catalog Co., New York.

<sup>2</sup> Harrison, *Phys. Rev.* **24**, 466 (1924).

ments of the transmission of sodium vapor. The vapor shows a sharp maximum absorption exactly at the limit  $1s \approx 2414\text{\AA}$  and a decreasing absorption toward both shorter and longer wave-lengths. The absorption at longer wave-lengths corresponds to the higher members of the principal series, while that at the shorter wave-lengths is evidence of photo-electric ionization.

The obvious difficulty in the direct determination of the photo-electric effect of vapors by ordinary methods employed for solids arises in the photo-electric emission from the electrodes produced by radiation scattered in the vapor. These electrodes are usually contaminated by the vapor, and since the threshold frequency for the material in the vapor state should be much greater than that for the liquid or solid phases and probably for adsorbed films, a slight contamination completely masks the true photo-electric emission from the vapor. Also, the threshold frequencies of most vapors should be considerably higher than those for electrode materials even when completely free from an alkali metal.

Williamson<sup>3</sup> reduced these difficulties to a minimum by projecting a jet of potassium vapor into a vacuum chamber, and past a carefully diaphragmed beam of ultraviolet radiation. The presence of positive ions in the illuminated stream was determined by the use of accelerating and retarding electric fields. Since the amount of ionization produced is extremely small, very sensitive measurements with a Compton electrometer were required, and, in order to obtain high intensity of illumination, a Cooper-Hewitt arc with ultraviolet filters was employed. The ionization with filters cutting off different portions of the ultraviolet indicated that the positive current began somewhere between 2800 and 3100 $\text{\AA}$  while  $1s$  for potassium corresponds to 2856 $\text{\AA}$ . Samuel<sup>4</sup> confirmed this work with measurements of which the following are typical. Current in amperes  $\times 10^{-13}$ : no illumination .7; illumination 1.7; with filter transmitting to  $\lambda 2804$ , 1.5; with filter transmitting to  $\lambda 2893$ , 0.7.

Kunz and Williams,<sup>5</sup> using a beam 80 $\text{\AA}$  wide from a quartz spectrograph mounted as a monochromator, a quartz arc as source and a three-electrode tube in which the electrodes were exposed to scattered radiation, obtained, by electrometer drifts, an indication of a photo-electric ionization in caesium between 3140 and 3220 $\text{\AA}$ . As will be apparent from the results discussed below, the interpretation of the data obtained by these investigators is open to question. If the observed current was not due to

<sup>3</sup> Williamson, *Phys. Rev.* **21**, 107 (1923).

<sup>4</sup> Samuel, *Zeits. f. Physik* **29**, 209 (1924).

<sup>5</sup> Kunz and Williams, *Phys. Rev.* **22**, 465 (1923).

photo-electric emission from the electrodes, it may have been a true photo-electric emission from the vapor excited by the intense 3130 group in the Hg source. Under these circumstances, and provided satisfactory resolving power was employed, spectral energy curves similar to that in Fig. 3 of the present paper should have been obtained. At any rate, an accurate determination of the caesium limit cannot be made with the radiation from a mercury arc since there is very little radiation between 3340 and the intense group at 3130A, while the theoretical limit for caesium is 3184A.

The most recent contribution by Lawrence<sup>6</sup> reopens the entire subject. A method quite similar to Williamson's was employed but much higher precision is claimed and apparently obtained. He concludes that radiation of wave-length greater than 2610A produces no ionization in the jet of potassium vapor while the true photo-electric limit should be 2856A. Lawrence suggests that the effect observed was due to the presence of potassium molecules in the jet. Harrison and Slater, in a paper in this issue, have concluded from an investigation of the absorption spectrum that most of the atoms in rapidly distilling sodium vapor are in molecular

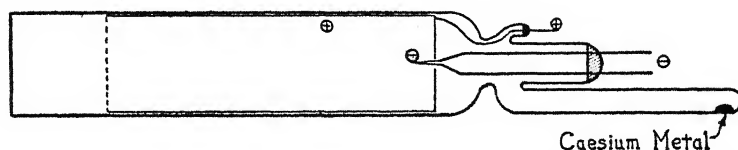


Fig. 1. Tube for measuring photo-ionization by the neutralization of space charge.

combination. If the interpretation of Lawrence be correct the present status of the subject, as far as the direct determination of the photo-electric effect in monatomic vapors is concerned, remains about as described in "The Origin of Spectra."

#### DESCRIPTION OF THE METHOD

In this paper a new method for the measurement of the photo-electric effect in vapors is described which is far more sensitive than any heretofore applied and which is free from difficulties due to scattered radiation. The design of the tube is illustrated in Fig. 1. A small tungsten filament is mounted on the axis of a platinum cylindrical electrode which is closed at the back except for a small hole through which the filament protrudes, and is closed at the front end by a coarse grid. The con-

<sup>6</sup> Lawrence, Abstract in Phys. Rev. 25, 584 (1925); complete paper to appear in Phil. Mag. The writers express their appreciation for the opportunity of reading this paper in the manuscript.

taining tube is of quartz with a flat quartz window fused to the front and tungsten-glass seals at the back fused in by the use of a quartz-Pyrex graded seal. After thorough baking to remove mercury vapor, caesium metal was distilled in, and the tube was sealed off from the pump. It was then mounted in an oven the temperature of which could be regulated to give the desired vapor pressure. Radiation from various sources such as a concentrated-filament tungsten lamp, mercury arc, etc., was analyzed by a quartz monochromator and directed into the cylindrical enclosure. This was maintained at a potential slightly positive to that of the hot wire. The latter was so operated that the thermionic current was normally limited by the negative space charge, so that the formation of ions by any method tended to neutralize this space charge and permit the flow of more electrons from the wire. Kingdon<sup>7</sup> and Hertz<sup>8</sup> discovered this method independently of each other and applied it for the detection of ions produced by electronic bombardment. However, Kingdon considered the subject in much greater detail and pointed out just why the method is capable of such extreme sensitivity. In general, the ion will possess a tangential velocity component, on account of its thermal agitation. It is repelled by the positively charged outer electrode but like a comet entering our solar system, cannot fall into the negatively charged wire, provided this is of sufficiently small dimensions, since it possesses angular momentum with respect to the wire. In a high vacuum the ion therefore traverses a rosette-shaped orbit about the filament and is imprisoned in the enclosure. When the vapor pressure is increased, the path of the ion is, of course, altered by collision; however, the imprisonment effect still exists. On account of the low mobility of an ion compared to an electron, each trip across the tube neutralizes the space charge of from 100 to 800 electrons, depending upon the vapor. Kingdon actually detected as many as 350 trips so that the high sensitivity of the method is apparent.

Foote and Meggers<sup>9</sup> in 1920 pointed out that a comparatively cool metal surface in the presence of caesium vapor is a copious source of electrons. The explanation of this phenomenon in connection with the work function of the metal is due to Langmuir and Kingdon<sup>10</sup> who have completely developed the theory and use of caesiated filaments. At temperatures below a red heat tungsten in the presence of caesium gives electron currents as high as 0.3 amp./cm<sup>2</sup>. The tungsten filament used

<sup>7</sup> Kingdon, *Phys. Rev.* **21**, 408 (1923).

<sup>8</sup> Hertz, *Phys. Zeits.* **18**, 307 (1923).

<sup>9</sup> Foote and Meggers, *Phil. Mag.* **40**, 94 (1920).

<sup>10</sup> Langmuir and Kingdon, *Phys. Rev.* **21**, 380 and 381 (1923); *Science* **57**, 58 (1923).

in the present work was about 0.015 cm in diameter and 2 cm long. The saturation current was therefore of the order 28 m-amp., while the current limited by the space charge may be roughly estimated from the equation for the current to a long cylinder from a wire along the axis,<sup>11</sup> as follows:

$$i = \frac{2\sqrt{2}}{9} \sqrt{\frac{e}{m}} \frac{lV^{3/2}}{r\beta^2} = 14.68 \times 10^{-6} \frac{lV^{3/2}}{r\beta^2} \text{ amperes.}$$

Here  $l$  is the length of the cathode,  $r$  the radius of the cylinder,  $V$  the potential in volts and  $\beta$  a complicated function of  $r/r_0$  where  $r_0$  is the radius of the cathode. The quantity  $\beta$  is nearly unity,  $l=2$  cm;  $r=1.5$  cm so that  $i$  at 2 volts is computed to be  $5.5 \times 10^{-5}$  ampere; our observed value was  $5 \times 10^{-5}$ , assuming an initial correction of one volt.

Langmuir and Kingdon have shown that on account of the low ionization potential of caesium and the high work function of tungsten, caesium atoms, evaporated from the filament, leave as positive ions. In order to avoid the neutralization of the space charge by this effect it is essential to operate the filament at as low a temperature as possible. On the other hand the temperature must be sufficient to give a thermionic current which is limited by space charge. There is, accordingly, only a narrow range of filament temperatures over which the tube is a sensitive detector for photo-electric ionization. No difficulty was experienced from this source, but had there been trouble a filament of lower work function might have been utilized.

Since the current without illumination of the vapor is limited by the negative space charge, any ordinary photo-electric emission from the walls or even from the filament itself has no effect.<sup>12</sup> The tube is sensitive only to the presence of positive ions.

#### ILLUMINATION WITH UNRESOLVED RADIATION

A preliminary test of the method was made by the use of the direct radiation from a quartz mercury Labarc, and current-voltage curves were obtained for various filament temperatures and vapor pressures of caesium, both with and without radiation. The increase in thermionic

<sup>11</sup> Langmuir and Blodgett, Phys. Rev. **22**, 347 (1923).

<sup>12</sup> This statement assumes the validity of the simple space charge equation in which initial velocities are neglected. Some of the photo-electrons liberated by quanta of frequency very much higher than the photo-electric threshold of the metal may have velocities sufficient to carry them through the space charge. Under our working conditions this contribution to the observed current was negligible. The total photo-electric current from the cold filament was less than  $10^{-8}$  ampere even with the unresolved radiation from the mercury arc.



current when radiation is directed into the tube becomes greater the higher the vapor pressure and the larger the filament emission. Changes of more than a milli-ampere were observed, and the tube characteristics indicated that much larger effects could be secured under easily realizable experimental conditions.

Fig. 2 shows a group of current-voltage curves with and without radiation and with several filament temperatures. The tube was operated at  $135^{\circ}\text{C}$ , giving a vapor pressure of about 0.007 mm Hg. The section

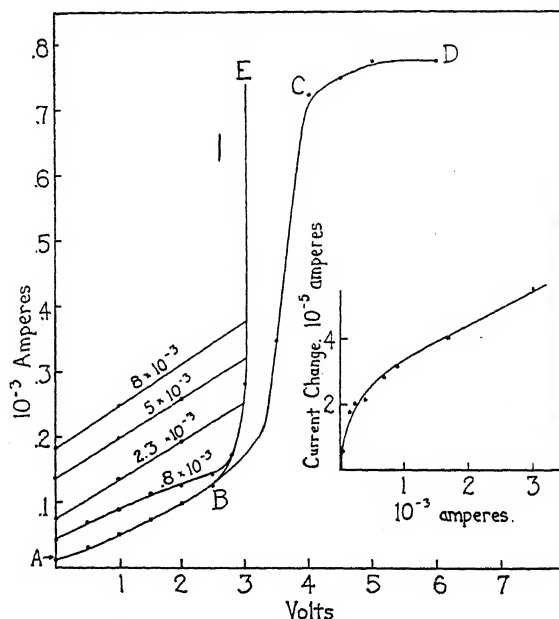


Fig. 2. Current voltage curves in caesium vapor at  $135^{\circ}\text{C}$ . *ABCD* and *ABE* represent thermionic currents for different filament temperatures, without illumination. Curves above *AB* show currents with the vapor illuminated by a mercury arc. Saturation for the filament emission is indicated by the figures over each curve. The inset shows the photo-ionization effect as a function of filament emission.

*AB* of the lower curve represents the current as limited by space charge without illumination, and was practically the same for all the filament temperatures employed. Near *B* at an applied potential of about 2.7 volts, ionization by electron impact begins. There is an initial potential correction of about 1 volt. The section *BCD* represents the current-voltage relation for only the lowest filament temperature. This current approaches a nearly constant saturation value below 6 volts. At higher temperatures of the filament the current rises more rapidly from *B*, reaching saturation at approximately the same voltage at a point far

above the scale of the drawing. The section *BE* represents roughly the initial rise for all other filament temperatures. The curves above and approximately parallel to *AB* were obtained with illumination from the arc, the figures over each curve giving the saturation current above the ionization potential. The *change* in current with radiation is nearly independent of the voltage below the ionization potential but rapidly approaches zero when ionization by electron-impact occurs. The manner in which the *change* in current due to radiation increases with the emissive power of the filament is illustrated by the inset of Fig. 2, which gives the change in current at 1 volt applied potential as a function of the saturation current. The change in current, due to radiation, as a function of the vapor pressure of the caesium, is illustrated by Table I. These values apply for a saturation current of  $2 \times 10^{-4}$  ampere. The actual current at 1 volt, as limited by space charge, was  $5 \times 10^{-5}$ . The ratio of the currents with and without radiation was purposely made small.

TABLE I

*Change in current due to radiation as a function of vapor pressure.*

Temperature	Pressure <sup>13</sup>	Change in current
95°C	0.64 bars	$0.7 \times 10^{-5}$ ampere
108	1.5	1.1
135	9.7	2.0
145	12.	2.2
170	43.	3.2

For the sensitive detection of radiation the relative change in thermionic current should be as large as possible. The curves in Fig. 2 show that, other conditions remaining constant, the ratio of the currents with and without illumination increases as the potential decreases. The most satisfactory sensitivity was obtained when the outer electrode was slightly less than 1 volt positive to the effective portion of the filament, which in view of the 1 volt initial correction, required a few tenths of a volt negative applied potential. The curves of Fig. 2 show an increase in sensitivity with filament temperature but, as already pointed out, there is a sharp limitation to this relation when an appreciable evaporation of ions occurs. It was found advisable to operate the filament at about 700°C.

#### MONOCHROMATIC ILLUMINATION

A Hilger ultraviolet monochromator with an aperture ratio of about *f*7 at  $\lambda 3000$  was employed. Both slits were set at 0.01 inch for most of the work. The caesium tube was heated to 180°C, corresponding to a vapor

<sup>13</sup> Langmuir and Kingdon, Proc. Roy. Soc. 107A, 61-79 (1925).

pressure of 0.045 mm Hg. The filament temperature was adjusted for a saturation current of 0.01 ampere and the applied potential was  $-0.5$  volt. When especially high sensitivity was required the thermionic current without illumination, of the order  $10^{-6}$  ampere, was compensated by a potentiometer circuit.

The photo-electric ionization by the mercury arc is shown in Fig. 3. The lower curve gives the increase in current as a function of wave length, in this particular case amounting to  $6 \times 10^{-7}$  ampere at  $\lambda 3130$ . Superposed on the curve is a plot of the mercury spectrum. The upper curve gives for comparison radiometric data roughly copied from a

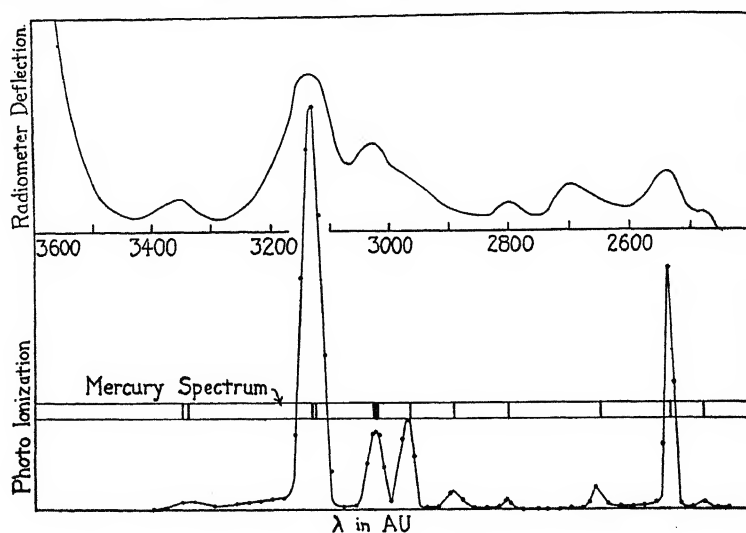


Fig. 3. Lower curve shows change in current with illumination by mercury arc lines as a function of the monochromator setting. Vertical lines superposed on this curve show the positions of the strong arc lines. The upper curve is a rough copy of radiometric data for the mercury arc.

paper by Harrison and Forbes.<sup>14</sup> The two sets of data are, of course, not strictly comparable. The photo-electric ionization is almost zero for wave-lengths greater than 3130 but is well pronounced for this group and for the mercury lines of higher frequency. As already mentioned, the mercury spectrum is deficient in radiation near the  $1s$  limit for caesium ( $\lambda 3184$ ) and hence is not at all a suitable source of radiation for the present requirements. However, the small current observed between  $\lambda 3130$  and  $3400$  is a true photo-electric effect, as is demonstrated later, and is not due to scattering of radiation by the monochromator.

<sup>14</sup> Harrison and Forbes, *J.O.S.A. and R.S.I.* 10, 1-18 (1925).

Curve I of Fig. 4 illustrates the effect observed when a 600 watt glass Mazda lamp was used as a source, the slit width, 0.01 inch, being the same as for Fig. 3. The absorption of the glass is practically complete near 3000A. The energy distribution of this source was roughly estimated by assuming that the tungsten radiated as a gray body at 2700°C and

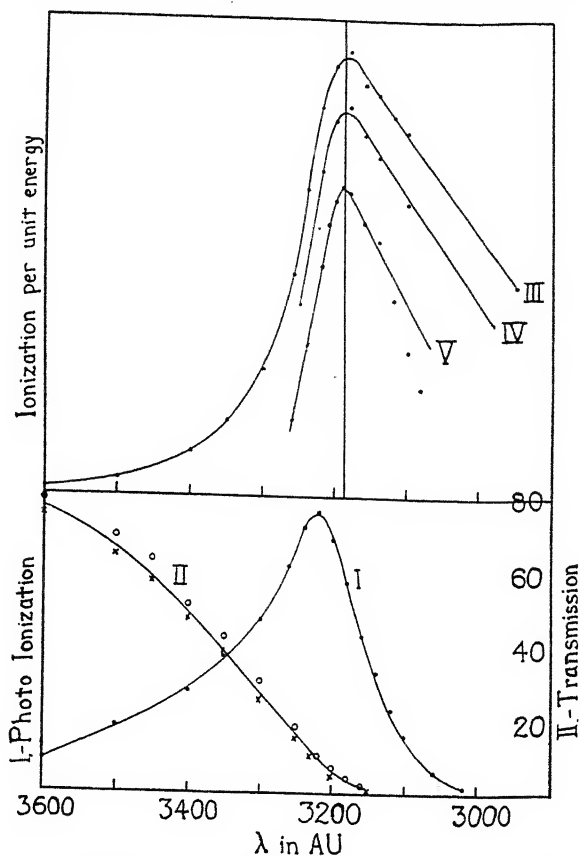


Fig. 4. I. Change in current versus wave-length for illumination by a mazda lamp. II. Transmission of sample of glass; circles determined by photo-ionization; crosses by standard method. III, IV and V. Radiation effect per unit radiation energy. The upper base line is the zero for III.

the values so obtained were corrected by use of spectrophotometric data on the transmission of the glass from a similar lamp. These data were further corrected for the dispersion of the monochromator. Curve III, thus derived from Curve I, shows the radiation effect per unit energy flux from the monochromator, and Curves IV and V represent similar but independent experimental data.

The form of these curves was at first surprising. While the maximum ordinate almost exactly coincides with the limiting frequency  $1s$ , the decrease to the left of the maximum is not nearly so rapid as should be expected if there existed for the vapor a sharply defined photo-electric threshold. On the long wave-length side of this threshold value the drop from the maximum should be just as abrupt as for a strong monochromatic line such as  $\lambda 3130$  in Fig. 3.

While Fig. 3 shows no evidence for impurity due to scattering by the monochromator system the following test was made with the mazda lamp as source. The photo-electric ionization effect was measured at various wave-lengths with a sample of glass of known transmission interposed and removed. From these observations the effective transmission coefficient of the glass was obtained. The results of this method are plotted as circles in Curve II of Fig. 4 while transmissions by a standard spectrophotometric method<sup>15</sup> are indicated by crosses. The agreement is quite satisfactory. The transmission at  $3184\text{\AA}$  is less than 5 percent so that scattered light of shorter wave-length would have been almost completely absorbed, thus making our observed transmissions too low. This confirms the existence of a photo-electric effect for the longer wave-lengths and incidentally suggests that the tube employed may prove useful in ultraviolet photometry and intensitometry.

The form of the photo-ionization curve on the short wave-length side is not so certain. The computation of the energy distribution is unreliable near the transmission limit of the glass. The acetylene flame was found too weak for precise measurements although one point at  $2950\text{\AA}$  has been plotted on Curve III. A straight line has been drawn through all the values for wave-lengths less than  $3160\text{\AA}$ , but evidently this linear relation cannot be extrapolated since the sensitivity at  $2537$  is comparatively high, as shown by Fig. 3.

#### INTERPRETATION OF RESULTS

Curve I of Fig. 5 illustrates the type of absorption observed near an x-ray limit. With high resolving power the edge of the band at the limit is sharply defined and there is satisfactory evidence that the energy absorbed is expended in ionization in the manner required by the Einstein photo-electric equation. Curve II illustrates the type of absorption observed near the limit  $1s$  of the principal series of an alkali vapor. This is a schematic adaptation for caesium of data for sodium by Harrison.<sup>16</sup>

<sup>15</sup> These measurements were made by Dr. K. S. Gibson of the Colorimetry Section, Bureau of Standards.

<sup>16</sup> Harrison, *Phys. Rev.* **24**, 466-77 (1924).

The unresolved line absorption on the long wave-length side merges into the continuous absorption beyond the limit so that the general appearance of the curve is quite different from that obtained in the x-ray region. Interpreted on the basis of Bohr's theory, the absorbed energy of frequency higher than the limit  $1s$  produces ions; the absorption of lower frequencies produces atoms in various states of excitation. These

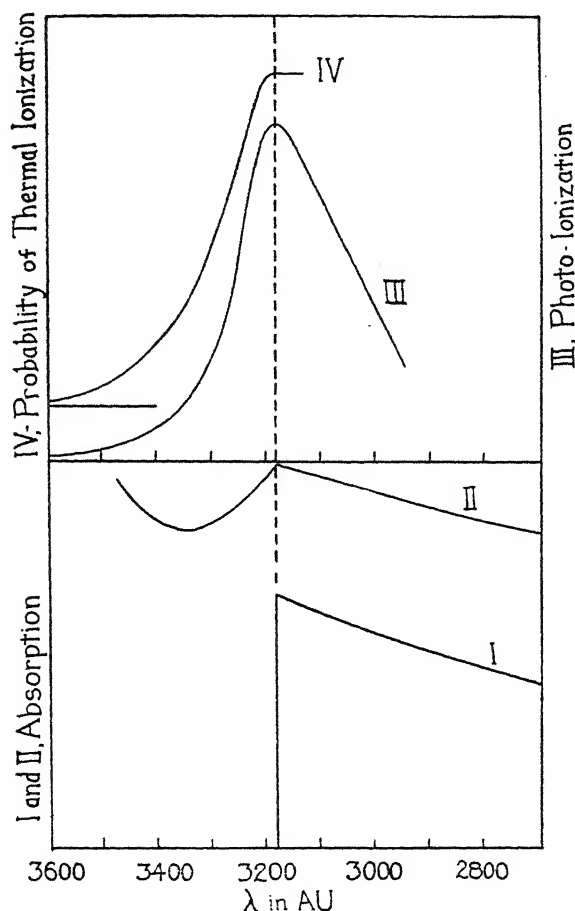


Fig. 5. I. Variation of absorption with wave-length near x-ray limit. II. Absorption near  $1s$  limit of an alkali vapor. III. Photo-ionization effect. IV. Probability of ionization from an  $mp$  state by atomic collision at  $180^\circ\text{C}$  as a function of wave-length  $1s \rightarrow mp$ .

latter being neutral should not be detected by the present method of analysis so that unless some secondary process occurs, the drop in the photo-ionization curve should be abrupt as in the case of an x-ray limit.

The secondary phenomenon effective is the ionization by collision of excited atoms.

At the temperatures and pressures employed in this experiment the average duration of the mean free path of a normal caesium atom is comparable with the life of an atom in an excited state.<sup>17</sup> Since the size of an atom rapidly increases for the higher stages of excitation, the mean period becomes smaller, and in general an excited atom will collide with another atom before it has had time to radiate. The relative kinetic energy of the two colliding atoms may suffice to complete the process of ionization. Thus, a collision at the r.m.s. speed for 180°C involves kinetic energy sufficient to ionize a caesium atom in the  $15p$  state, a state which is produced by the absorption of 3231Å, nearly 50Å beyond the proper threshold value. From simple kinetic theory, the fraction  $F$  of the total number of collisions in which the translational energy of one atom relative to the other is greater than  $E_0$  ergs has the form

$$F = [1 + (3.64/T)E_0 \cdot 10^{15}]e^{-(3.64/T)E_0 \cdot 10^{15}}.$$

If  $E_0$  represents the work required to ionize a caesium atom from an excited  $p$  state, one finds, for example, that 93 percent of the collisions at 180°C may produce ionization from the  $20p$  state, the latter condition following the absorption of  $\lambda 3210$ . Similarly, 30 percent of the collisions may effect ionization from the  $8p$  level, this state following absorption of  $\lambda 3348$ . Curve IV of Fig. 5 shows the fraction  $F$  plotted against the wave-length  $1s \rightarrow mp$ . It therefore represents a controlling factor in the probability of ionization from an  $mp$  state produced by absorption of the radiation  $1s \rightarrow mp$ . This incomplete probability function has almost exactly the same form as the observed photo-ionization data, Curve III. The two graphs have been displaced vertically to avoid confusion. The quantitative agreement is fortuitous, since several factors entering into the exact form of the probability curve have not been considered; for example, the absorption coefficient of the vapor, the life and the mean free path or time of an excited atom. However, the computations show at least qualitatively that interatomic collisions can account for the observed ionization on the long wave-length side of the threshold.

These considerations show that the setting in of ionization whether by radiation or by electron impact cannot be sharply discontinuous under any effective experimental conditions. Much lower pressure, and resulting decrease in sensitivity, may make ionization by interatomic collision inappreciable, but even then photo-ionization by infrared radia-

<sup>17</sup> Estimated as  $1.4 \times 10^{-8}$  sec. for sodium; cf. Ellett, J.O.S.A. and R.S.I. 10, 437 (1925).



tion may play an important rôle. The radiation corresponding to the maximum intensity from a black body at  $180^{\circ}\text{C}$  has a frequency sufficient to ionize a caesium atom from the  $8p$  state.

An investigation of the relative importance of the ionization of excited atoms by heat radiation and by interatomic collision will require data similar to Fig. 4 for various pressures and temperatures. It is important to investigate the exact form of the photo-ionization curve on each side of the maximum. Possibly with higher resolution the curve on the long wave-length side will show secondary peaks corresponding to the successive members of the principal series. It is evident that the general method described is applicable to many problems in cumulative ionization.

In conclusion, the writers desire to thank Dr. Sebastian Karrer of the Fixed Nitrogen Laboratory for the loan of the quartz monochromator and Mr. R. L. Chenault for assistance in making the observations.

BUREAU OF STANDARDS,  
WASHINGTON, D. C.  
May 15, 1925.

## THE RELATIVE IONIZATION IN DIFFERENT GASES FOR SLOW-MOVING ELECTRONS

BY WILLIAM P. JESSE

## ABSTRACT

A uniform beam of electrons was obtained by allowing thermions from a tungsten filament to fall through a given potential difference between the filament and a perforated plate and to pass through the plate into a short region devoid of strong electric fields. There, due to the energy acquired, they ionized the gas present, the positive ions being caught on a concentric ring element and the electrons themselves on a plate opposite the perforated plate. With the pressure low enough to prevent secondary effects the ionization was determined for electron energies ranging from 20 to 300 volts. With increasing electron energies the ionization in each gas was found to reach maximum at the following voltages: for He 140, Ne about 220, A 100, CO 120 and N<sub>2</sub> 100 volts. For 200 volts the relative ionizations at 1 mm pressure, with reference to that in Ne taken as 1.0, are: H<sub>2</sub> .91, He .48, CH<sub>4</sub> 3.5, N<sub>2</sub> 3.2, CO 3.45, A 4.1. The results are in good agreement with those of Hughes and Klein, except that the value for argon is 0.7 higher. A second maximum was observed in each case at 350 to 400 volts which was probably due to secondary rays, but is not completely understood.

RECENTLY Dushman<sup>1</sup> and Found from their studies with the ionization gauge, using potentials between 125 and 250 volts, have concluded that, in general, ionization by electrons in various gases is approximately proportional to the number of electrons in their respective molecules. This result is rather surprising and difficult to understand because it implies that the chances for ionization depend only on the total number of electrons, irrespective of the fact that the energy necessary to knock out an electron from various atoms and from different parts of the same atoms, varies greatly. It seemed desirable, therefore, to study this result using slow-moving electrons of constant velocity throughout their path. After the investigation reported in this paper was completed, a paper by Hughes<sup>2</sup> and Klein dealing with the same subject, appeared. The results in general confirm those of Hughes and Klein, but differ in some respects. The method used differs from theirs in that the ionization was produced by electrons of approximately constant velocity.

<sup>1</sup> Dushman and Found, *Phys. Rev.* **23**, 734 (1924); also Dushman, *The Production and Measurement of High Vacuum*, *Gen. Elec. Rev.* (1922).

<sup>2</sup> Hughes and Klein, *Phys. Rev.* **23**, 450 (1924).

The general method employed was to obtain electrons of uniform velocity by allowing thermions to fall through a given potential difference, and then to pass these into a region devoid of strong electric fields, where owing to their speed, they were able to produce ionization in the gas present. The electrons themselves and any negative ions formed were collected on a plate and the positive ions, produced in the given region, were caught on another collector. For a given accelerating potential and gas pressure, the ratio of the positive ion current to the electron current gives a measure of the ionization in any particular gas. For a given gas the ionization could also be obtained as a function of the accelerating potential.

In order to observe the ionization due to the primary electrons alone, it was essential to use very low gas pressures, from 1 to  $200 \times 10^{-5}$  mm. Under these conditions only one in a large number of primary electrons actually made an ionizing impact. For the same reason the ionization produced by secondary electrons ejected from the atoms of the gas was a negligible part of the whole. The space charge in the region considered was kept quite low by using electron currents of the order of 20 micro-amperes.

#### APPARATUS

After a preliminary trial of tubes of various designs, the following type was adopted (Fig. 1). The tube itself was 8 cm in diameter and was made of Corning G-702-P glass. The source of electrons was a tungsten filament *T*, welded to tungsten leads 1 mm in diameter. The filament was enclosed in a molybdenum cylinder *C*, 2 cm in diameter, and was placed close to a small circular hole through which the electrons passed. The diameter of this hole was 1.5 mm. The plate *P* was of molybdenum, and the collector *M* for positive ions was a tungsten wire bent to form a circle around the aperture. To protect the collector from the possibility of direct impact from electrons, a small cylinder was spot-welded to the larger cylinder and completely surrounded the hole. In most of the experiments, the distance from the plate to the top of the small cylinder was 7 mm, and this was considered the length of path from which positive ions were gathered. All the elements in the tube were supported by double leads in order that the latter might be further heated by an electric current during the process of baking the tube.

The tube was directly attached to a liquid air trap which was connected to a McLeod gauge and could be connected to a diffusion pump. A pressure as low as  $10^{-5}$  mm could be read easily on the gauge. The apparatus

other than the tube was made of Pyrex glass so that it might be heated to drive off gases and moisture from the walls.

*Electrical connections.* During all the experiments the positive terminal of the filament was kept grounded. The cylinder and plate were maintained at the same potential and the combination was always kept positive with respect to the filament. The collector of positive ions

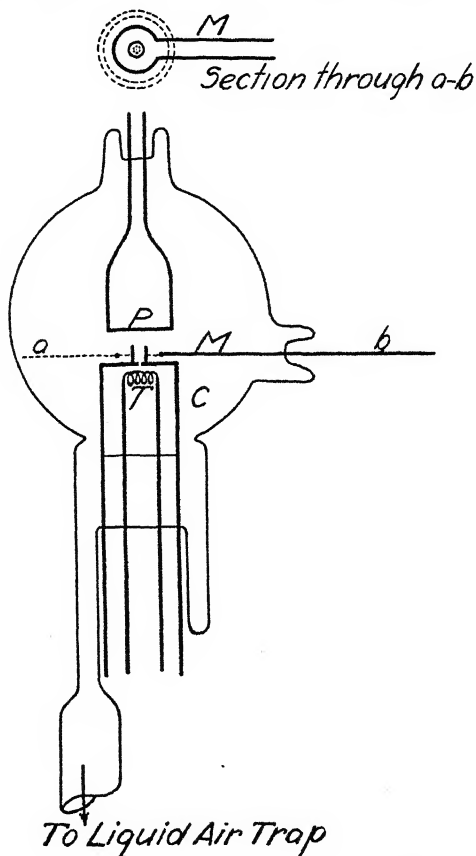


Fig. 1. Diagram of experimental tube.

was kept negative with respect to the filament. The electron current to the plate *P* was measured with a micro-ammeter, the positive ion current to the collector with a high sensitivity galvanometer. These instruments were calibrated from time to time during the course of the experiment.

*Preliminary manipulation.* The apparatus was so constructed that all parts could be surrounded by electric ovens and baked at a temperature of 450° C. As a rule such a general heating was necessary only occasion-

ally. Before every series of runs, however, the oven was placed over the tube and liquid air trap with only a few inches of the latter projecting beneath, and a temperature somewhat below the softening point of the glass was maintained for half an hour. The lower end of the trap was then immersed in liquid air and the heating continued for another half hour. During this latter period all the tungsten leads in the tube were heated to a dull red heat by means of an electric current, and a hand torch was played upon all parts of the apparatus outside the oven. The oven was then removed without disturbing the liquid air trap. Next the tube elements were heated to a bright red heat by means of a

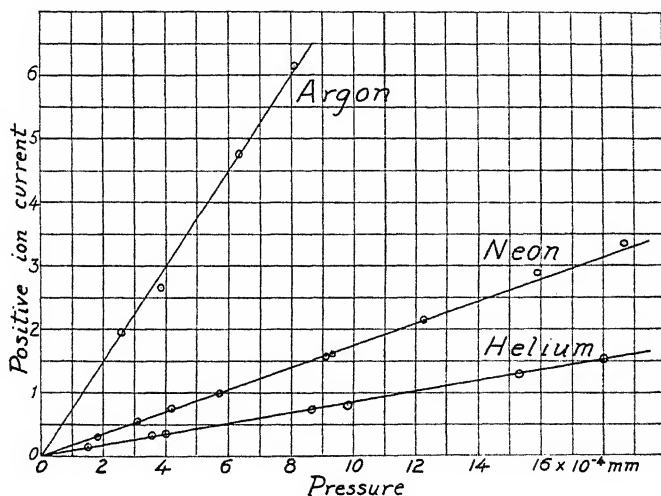


Fig. 2. Relation between positive ion current in galvanometer divisions and pressure, with 200 volts accelerating potential.

high frequency inductive-heating device, and then the trap was submerged as deeply as possible in the liquid air. During the course of the experiments the liquid air was always kept at this latter level.

In order to determine the efficacy of the treatment described above, control runs were taken during the course of the experiments to test for an evolution of gas from the apparatus. The system was pumped out and sealed off, and the filament allowed to remain lighted for a time equal to the average time of a run. No evidence of an evolution of gas was perceptible either by the McLeod gauge or by the registering of a positive ion current by the galvanometer.

#### OBSERVATIONS

The ionization in a gas was measured under two different sets of conditions—(1) when all quantities were kept constant except the pressure

(Figs. 2, 3); and (2) when all quantities were kept constant except the accelerating potential for the electrons (Figs. 4 and 5). In the first of these series of observations the cylinder and the plate were kept at the same potential of 200 volts positive with respect to the filament and the collector of positive ions 40 volts negative with respect to the filament. The electron current to the plate was kept constant by regulating the temperature of the filament. The pressures were read with the McLeod gauge, and the corresponding positive ion currents with the galvanometer.

Since the collecting ring drew positive ions from the region between the cylinder and plate, one might expect the energies of the ionizing electrons to be modified to a certain extent by the field due to the collector. To determine whether this introduced a serious error, preliminary runs

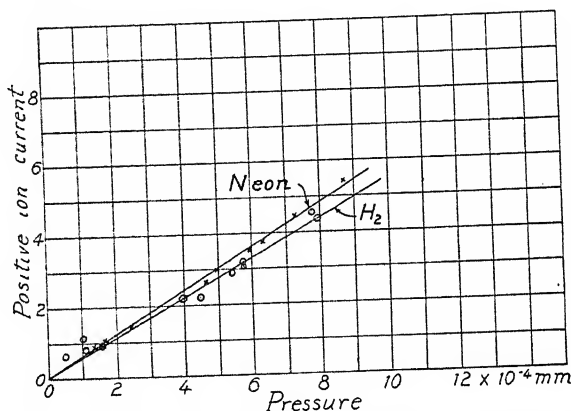


Fig. 3. Relation for hydrogen and neon between positive ion current, in galvanometer divisions, and pressure, with 200 volts accelerating potential.

were made with the collector at different negative potentials. These varied from  $-5$  to  $-40$  volts with respect to the filament. If the field due to the collector had much effect in accelerating the electrons, the curves shown in Figs. 4 and 5 should be shifted along the voltage axis as the collector potential was changed. No such shift was observed. The maximum with  $-5$  volts was the same as for  $-40$  volts. Moreover no important change was apparent in the early portion of the curves where the ionization changes rapidly with small changes in accelerating potential. The only difference between the curves taken at  $-5$  and at  $-40$  was that the ordinates throughout the latter were a few percent greater than in the former. Since no shift was observed on thus changing the collector potential, it was considered that, though a small field did exist between the cylinder and the plate due to the collector, the effect

of this field in accelerating the ionizing electrons introduced no serious error.

With the pressure of the gas so low that the electron in its passage could make ionizing impact with no more than one molecule, the positive ion current should be directly proportional to the pressure, and this was found to be the case, as is shown in Figs. 2, 3. In these experiments the value of the positive ion current was from 1/100 to 1/1000 of the electron current, so the chance of a second ionizing encounter was negligible. The effect of the ionization produced by the ejected electrons was, for the same reason, negligible.

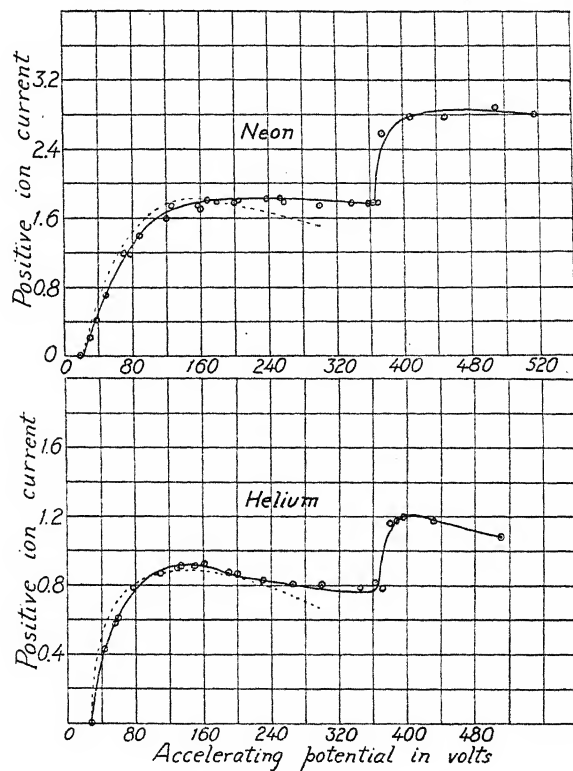


Fig. 4. Relation between positive ion current and electron energies in volts; pressure .001 mm.

When the speed of the electrons was varied by changing the accelerating potential and the other conditions were maintained constant the curves in Figs. 4 and 5 were obtained. These have all been reduced to a common pressure of 1/1000 mm. The ionization is seen to increase rapidly at first and after rising to a maximum to decrease slowly until



a sudden second increase takes place. The cause of the second sharp rise will be discussed later.

*The neon* used was obtained from the Linde Air Products Company and was considered by them to be very pure. It was examined spectroscopically in this Laboratory, especially with regard to the presence of helium, and neither visual observation nor a photograph gave any indication of impurities. Since neon was found to give quite consistent results, it was chosen as a reference gas and the relative ionizations in other gases were reckoned in terms of it. It may be said that the ratio between the ionization in two different gases was much more constant than the absolute magnitude of the ionization in either one. Once or twice it was necessary to open the tube to replace a burned out filament or for some other cause, and it was not possible to replace the elements in exactly the same position. This introduced a measure of uncertainty in the estimation of the length of electron path from which positive ions were drawn. Such a variation should affect the absolute values but not the relative values. The agreement obtained for the latter throughout the experiment was always very good.

The ionization voltage curve for neon, beginning at 20 volts, shows a gradual rise up to 150 volts and then an almost horizontal portion with an ill-defined maximum at about 220 volts.

*The helium* was purified by repeatedly passing it over charcoal immersed in liquid air until the spectrum showed nothing but sharp lines against a black background. Helium gave the least ionization of any gas used, the average ionization at 200 volts with respect to neon being 0.487. The curve for varying electron energy shows no ionization until 28 volts is reached. There is then a rise, sharper than in the case of neon, up to a maximum at 140 volts.

*The argon* used was obtained from the Nela Research Laboratory and originally contained something less than one-half percent of impurities. It was further purified by the action of an arc between calcium electrodes. The ionization in this gas was found to be quite large. The value at 200 volts, determined from a number of trials, was 4.15 times that with neon under the same conditions. With increasing electron energies ions were first formed at 18 volts and a maximum ionization was obtained at 100 volts.

*Carbon monoxide* was prepared by heating recrystallized oxalic acid in a glass tube. The water and  $\text{CO}_2$  were removed by passage through phosphorus pentoxide, finely divided potassium hydroxide, and lastly

through a liquid air trap. The ionization of carbon monoxide at 200 volts was to that of neon in the ratio of 3.45 to 1. Ionization first became apparent at 20 volts (Fig. 5), after which the curve rose rapidly to a maximum at 120 volts. The rate of decrease after this maximum was much greater than in the curves heretofore examined.

*Hydrogen* was prepared by the electrolysis of phosphoric acid and was thoroughly dried by passage through phosphorus pentoxide and a liquid air trap. The gas was most difficult to work with on account of the rapid "clean-up" effect of the tungsten filament. Nevertheless, for the

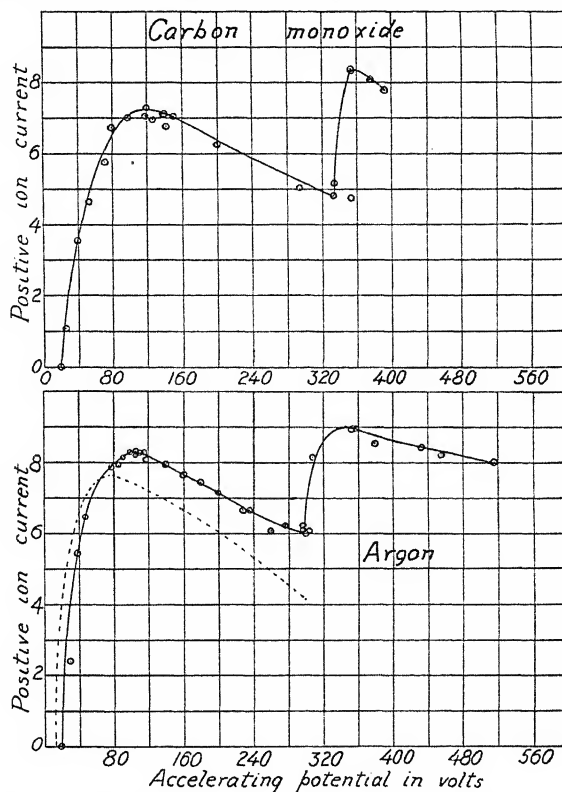


Fig. 5. Relation between positive ion current and electron energies in volts; pressure .001 mm.

ionization at 200 volts readings were obtained which leave no doubt as to the order of magnitude of the results (Fig. 3). Since the galvanometer sensitivity was quite different in this case, a neon curve is shown for reference. It may be noted that the ionization is not far different for the two gases. It was not possible to keep the pressure constant long enough to make a run with variable voltage.

*Methane* was prepared by a gentle heating of a mixture of sodium acetate and barium oxide. The resultant gas was passed over phosphorus pentoxide, potassium hydroxide, and through a trap immersed in liquid air. The ionization curve for 200 volts for this gas was almost coincident with that for carbon monoxide. The ionization relative to neon was found to be 3.50. An accidental contamination of the supply of gas prevented any trial being taken with varying electron energies.

*Nitrogen* was prepared by the action of bromine water on ammonium hydroxide according to a method devised by Waran.<sup>3</sup> The ionization at 200 volts was found to be 3.19 times that with neon under similar conditions. The "clean-up" effect in nitrogen, though smaller than in hydrogen, prevented the taking of as accurate a variable voltage curve as could be desired. However a maximum ionization was indicated at about 100 volts. Constant potential curves with varying pressures, similar to those taken at 200 volts, were also taken for this gas at 100 volts and 250 volts. The values obtained are given in the last column of Table I.

#### DISCUSSION OF RESULTS

It will be seen that all the variable voltage curves have the same general shape. The formation of ions begins when the accelerating potential for the electrons is equivalent to the ionization potential of the gas in question. It may be noted that these threshold values are in good agreement with more accurately determined values when we consider that no attempt was made to obtain extreme accuracy at this part of the curve.

The electron energies, expressed in equivalent volts, for maximum ionization in the different gases are as follows:

Helium	Neon	Argon	CO	N <sub>2</sub>
140	220	100	120	100

After the maximum is reached in each case, the ionization decreases as the energy of the ionizing electron increases, according to an almost linear relation. This decrease is not strange when we consider that there are two factors which play an important rôle in the process of removing an electron from an atom. The first of these factors is the energy of the impinging particle; the second is the time during which the particle is in the neighborhood of the electron to be removed. In the early part of the curve the first of these factors seems the predominant one and the ionization rises to a maximum as the energy of the particle increases.

<sup>3</sup> Waran, *Phil. Mag.* **42**, 246 (1921).

After this the chance of ionization seems more dependent upon the time factor, being smaller as the time of proximity between electron and atom decreases.

The sudden rise in the curves in the region of 300 volts is somewhat perplexing. It cannot be attributed to the beginning of ionization in another ring of electrons, since the position of the break may vary by twenty or thirty volts in different trials with the same gas and, moreover, occurs in helium which has no second ring of electrons. The ionization is therefore due most probably to some secondary emission in the tube itself.

If secondary electrons were emitted from the plate *P* (Fig. 1) under the bombardment of the primary electrons, they would give no effect until they had arrived at the energy required for ionizing the particular gas in the tube. As their energies further increased the ionization due to them would rapidly mount, and with still further increase in energy we should get a repetition of the primary ionization curve on a smaller scale. If a similar smaller curve were superimposed upon each of the main curves in Figs. 4 and 5, we should obtain approximately the results found experimentally. The varying position of the break for the same gas might, on this hypothesis, be attributed to changes in the surface of the plate produced by occluded gases, heat treatment and similar causes, which might affect the velocities of the emitted secondary electrons. In fact, it was observed that a prolonged glowing of the plate at a red heat had the effect of causing the break to move toward higher potentials.

The above explanation is not wholly satisfactory. It neglects the distribution in velocities of the secondary electrons and has other weak points. However, after carefully examining other possible causes, the writer is firmly convinced that the effect is due to ionization produced by secondary electrons from the plate, though perhaps not by precisely the process described above.

An attempt was made to estimate the amount of secondary emission from the plate by making the collecting ring positive with respect to it in a gas-free tube. For an accelerating potential of 280 volts a secondary electron current was obtained of about 12 percent of the primary electron current. Fully half of these electrons could be stopped by a retarding potential of 10 volts. No very satisfactory results could be obtained on account of the complication of tertiary electrons from the collector itself. Hence it is somewhat difficult to estimate the effect of secondary emission upon the measured ionization but it is believed to be small up to 300 volts.

THE RELATION BETWEEN THE RELATIVE IONIZATION AND THE NUMBER  
OF ELECTRONS IN THE MOLECULE

In Table I are collected the various values for the ionization relative to neon. Under each gas is given the ratio of its ionization to that of neon under similar conditions for the acceleration potential given in the first column of the table.

TABLE I

*Ionization relative to neon*

Accelerating potential	Neon	Helium	Argon	CO	H <sub>2</sub>	CH <sub>4</sub>	N <sub>2</sub>
200	1	0.487	4.15	3.45	0.91	3.50	3.19
200	1	0.472	3.93	3.46			....
50	1	0.661	9.18	6.23			....
100	1	0.563	5.47	4.60			3.93
250	1	0.447	3.54	3.12			3.02
300	1	0.437	3.34	2.86			....

In the first horizontal line of the table are given the ratios derived from the slopes of the linear ionization-pressure graphs, which were taken throughout at 200 volts only. These results are the most accurate of the whole investigation since they represent the average of quite a number of trials taken at this one voltage, and each trial gives the average of some six or eight plotted points. The trials checked among themselves within three or four percent.

In the second and succeeding lines of the table are recorded ratios obtained from the ionization-voltage curves (with the exception of those for nitrogen where on account of the troublesome clean-up effect ionization-pressure curves were taken for the voltages indicated). A strict proportionality between ionization and pressure has been shown to exist at 200 volts, and similar results were obtained for 100 and 250 volts. The values of the ratios given in the second and succeeding lines were taken from the curves shown in Figs. 4 and 5 and have been verified by other trials. Although this method does not yield results quite so accurate as

TABLE II

*Relative ionization divided by the number of electrons in molecule*

Accelerating potential	Neon (10)	Helium (2)	Argon (18)	CO (14)	H <sub>2</sub> (2)	CH <sub>4</sub> (10)	N <sub>2</sub> (14)
200	0.10	0.243	0.230	0.246	0.455	0.350	0.228
200	0.10	0.236	0.218	0.247			
50	0.10	0.331	0.510	0.445			
100	0.10	0.281	0.304	0.329	.....	.....	0.280
250	0.10	0.224	0.196	0.223	.....	.....	0.216
300	0.10	0.218	0.185	0.204			

those obtained from the slopes of the lines, nevertheless the agreement between the values in line two and line one is very good, the maximum variation being 5 percent.

In Table II are given the results of dividing the relative ionization values for each gas in Table I by the number of electrons in its molecule. If the ionization is proportional to the number of electrons, the ratio indicated should be a constant in each horizontal line. It is evident that such is not the case, the widest variations occurring in the cases of neon, hydrogen and methane. The values of ionization for hydrogen and helium have been observed by Dushman and Found with the ionization gauge to be approximately twice as great as the relation predicts. This is true for the writer's value of hydrogen but helium gives values quite in accord with the relation. The value for methane might perhaps be expected to be large since it contains four hydrogen atoms. However, Dushman and Found cite water vapor as giving values quite in accord with the relation, the number of electrons per molecule being taken as 10.

A glance at the curves of Figs. 4 and 5 shows that no constant ratio between the ionization in two different gases can exist which shall be independent of the accelerating voltages, for in such an event each curve must be the exact duplicate of the other save for the scale of the ordinates. On the contrary, the shapes of the curves are quite different. The maxima do not occur at the same points, neither are the rates of decline of ionization beyond the maximum the same in the various cases. Hence, it seems impossible that the direct proportionality between ionization and the number of electrons per molecule can be a general law.

Due to some uncertainty as to the exact length of path from which ions were collected the absolute values of the number of ions per electron per centimeter path are not considered very accurate. However, these values may be obtained for a pressure of 1 mm by multiplying the ordinates of the curves shown in Figs. 4 and 5 by the factor 1.75.

The writer's results are on the whole in fairly good agreement with the results of Hughes and Klein.<sup>2</sup> For 200 volts the following comparison is found between the relative ionizations with respect to neon.

	Ne	He	H <sub>2</sub>	CH <sub>4</sub>	A	N <sub>2</sub>
Hughes and Klein:	1	.472	1.016	3.53	3.44	3.47
Writer:	1	.487	.91	3.50	4.15	3.19

The maxima for ionization are obtained at the following voltages:

	He	Ne	A	N <sub>2</sub>
Hughes and Klein:	147	158	80	101
Writer:	140	220	100	100

The dotted curves in Figs. 4 and 5 are those of Hughes and Klein reduced to the same arbitrary scale as the writer's. Their neon curve was given the same maximum ordinate as the writer's and the ordinates

for the helium and argon curves were then plotted in the proper ratio to those of neon. This gives a comparison of the relative ionizations in the three gases rather than of the absolute values of the ionization.

It will be seen that the greatest difference between the results is in the case of argon. The table above gives for the relative ionization for argon at 200 volts a discrepancy of 17 percent. Although some values slightly lower than 4.0 were obtained by the writer for argon, none were obtained approaching 3.44. In this case, the writer would be inclined to favor his own value, since his argon (presumably derived from the same source) was further purified by means of a calcium arc. It seems very doubtful, however, whether the small impurity of 0.2 percent mentioned by Hughes and Klein would give the above difference, unless in the gas-flow method used by them the lighter impurity diffused into the ionization tube much more rapidly than the argon and thus gave effects greater than would be indicated by the original percentage of the impurity. The values for the relative ionization in helium, methane, nitrogen and hydrogen are in excellent agreement, especially considering the difficulties of working with hydrogen.

In comparing the values of Hughes and Klein with the writer's it may be seen that in the position of the maxima for ionization the values for neon are quite different. The greatest difference might be expected in this gas, since in both the investigations the curve for neon was found to be the most nearly horizontal, and hence the true position of the maximum the hardest to determine. No value was obtained by Hughes and Klein for the electron energy for maximum ionization in carbon monoxide. Here the writer's value of 120 volts compares favorably with the value of 125 volts given in an earlier paper by Mayer.<sup>4</sup>

In conclusion the writer wishes to express his thanks to Professor R. A. Millikan who suggested the problem and under whose direction the preliminary work was done, to Professor John Zeleny for aid and encouragement during the progress of the work, and to Dr. H. C. Rentschler of the Westinghouse Lamp Company for most generous help in the construction of the experimental tube and of the inductive heating system.

YALE UNIVERSITY,  
August 12, 1924.

<sup>4</sup> Mayer, *Ann. der Phys.* 45, 1 (1914).



## THE APPARENT TRANSMISSION OF LOW VELOCITY ELECTRONS THROUGH ALUMINUM FOIL

BY HENRY E. HARTIG

## ABSTRACT

**Apparent transmission of low velocity electrons through aluminum foil.**—Electrons were accelerated from a tungsten filament to a foil  $F$ .0003 cm thick behind which at a distance of 1 mm was a nickel receiving plate  $P$  connected to an electrometer. The ratio of electron current reaching  $P$  to that reaching  $F$  showed a maximum at about 8 volts primary energy though the position of this maximum shifted somewhat. By using a retarding potential on  $P$ , all the electrons reaching  $P$  were found to have velocities less than 10 volts (maximum number at about 2 volts) even when the primary bombarding electrons had a velocity of 1600 volts. Apparently, aluminum shows a transparent atom effect for slow electrons similar to that observed in rare gases. In addition to slow speed secondaries, the electrons reaching  $P$  include photo-electrons from the back side of  $F$  due to x-rays produced by the primaries. The effect with two foils was only  $10^{-4}$  times that through one and was probably largely photo-electric. The third foil cut down the plate current by an additional factor of 1/10.

**Critical potentials determined from photo-electric effect of soft x-rays from a metal foil.**—With a retarding potential (negative) on  $P$ , the plate current for primary velocities of over 40 volts is due chiefly to photo-electrons from the plate, while with two or three foils and an accelerating potential the current is due chiefly to photo-electrons from the back side of the foil. With aluminum, similar curves were obtained with one foil (negative  $P$ ) and with two and three foils (positive  $P$ ), showing breaks at a number of voltages including two at about 1490 and 1560 volts which correspond to  $K\alpha$  and  $K\beta$  lines of Al. No attempt was made to fix these breaks exactly but this method promises to be useful in studying critical potentials of metals.

RECENTLY, Schonland<sup>1</sup> and Terrill,<sup>2</sup> modifying Whiddington's earlier apparatus, and making use of the modern high vacuum technique, have again verified J. J. Thomson's formula for the loss in velocity suffered by cathode particles in passing through thin sheets of metal. Still more recently Terrill<sup>3</sup> has measured the absorption of cathode rays in aluminum sheets and incidentally has obtained additional confirmation of Thomson's formula. In particular he found that in order to pass through an aluminum foil .00031 cm thick, high speed cathode particles must have an incident velocity of at least 18.4 kv.

Both Schonland and Terrill found, however, that low velocity electrons, which they called secondary electrons, were present on the emer-

<sup>1</sup> Schonland, Roy. Soc. Proc. 104, pp. 235-247 (Sept. 1923).

<sup>2</sup> Terrill, Phys. Rev. 22, 101 (1923).

<sup>3</sup> Terrill, Phys. Rev. 24, 616 (1924).

gent side of a foil which was being bombarded, even when the incident velocity was less than the above-mentioned minimum. These secondary electrons could all be stopped by a retarding potential of 30 volts, and were excluded from the measured transmitted beam.

The investigation here described had for its object the determination of the origin, velocity distribution, and composition, of these so-called secondary electrons. It was planned to begin with very low incident electron velocities, increasing them until a measurable secondary current was obtained.

#### METHOD

Using modern high vacuum apparatus and an incandescent tungsten filament as a source of electrons, beaten aluminum foils, .0003 cm thick, were bombarded with electrons varying in velocity from zero to that acquired by falling through a potential of 1600 volts. The electrons proceeding from the other side of the foil were attracted to a collecting plate maintained at a positive potential with respect to the foil and connected to one pair of quadrants of an electrometer. A galvanometer connected to the foil measured the incident current. The ratio of the electrometer readings to the corresponding galvanometer readings was plotted against accelerating potential.

It was found that soft x-rays, generated by the bombarding electrons, were also transmitted through the aluminum foil. By maintaining the collecting plate at a negative potential of 30 volts, a current consisting of photo-electrons emitted by the plate could be made to flow in the opposite direction. The ratio of the secondary to the primary current was again plotted against accelerating potential.

In order to determine the velocities of the emergent electrons, a series of runs was made in which for constant accelerating potentials, the plate potential was varied from zero to increasing negative potentials and the ratios of the currents were plotted against retarding potentials.

#### APPARATUS

The final form of the tube adopted is shown in Fig. 1. It consists essentially of a Pyrex glass tube closed at one end by a brass plate *P* which is connected to the gauze inside the glass cylinder and is held in place, vacuum tight, by a mixture of beeswax and rosin. The side tube *F* contains the tungsten filament leads, the glass stopper and its lead-in tube *S*, the brass foil holder and supporting stem *H*. The stopper was ground into its seat and made vacuum tight with stop-cock grease. It was found from previous tube models that it was necessary to shield the nickel

receiving plate very carefully against multiply reflected electrons, for in the absence of high retarding fields, electrons were apparently diffused throughout the interior of the tube. Hence the electrometer shield was continued throughout the length of the brass lead-in tube. This is not shown in the figure. Special precautions were taken in the selection and mounting of the aluminum foils. The particular piece of foil chosen for a run was inspected as to freedom from holes by placing it in a darkened room before an opening in a box containing a 100 watt light. A copper ferrule tightly spun over the open end of the brass receiving chamber was used to hold the foil in position.

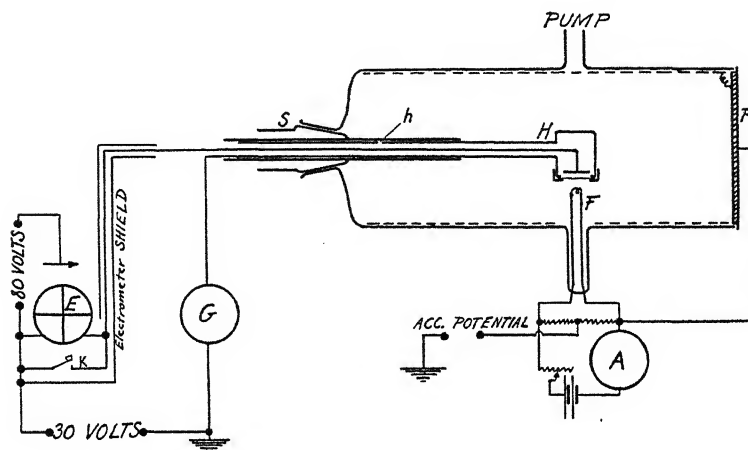


Fig. 1. Diagram of tube and electrical connections.

The brass lead-in tube was cemented with sealing wax to the outer end of the glass tube running through the center of the stopper. A hole  $h$  drilled through the brass tube about 3 cm back from the end of the glass tube, allowed the pressure on both sides of the foil to become equalized without presenting a free path for electron diffusion to the receiving plate.

During the outgassing process and glowing of the filament, the receiving chamber was rotated so that the foil faced away from the filament and thus contamination was prevented. Also by rotating the foil out of the incident electron stream during a run the fact that the current measured was actually coming from the foil could be checked.

The pump system consisted of a Langmuir mercury diffusion pump with a Gaede rotary and an oil fore-pump. A slush of carbon dioxide snow and acetone was used in the mercury vapor trap whenever the Langmuir pump was running.

A Leeds and Northrup galvanometer bridged with an Ayrton shunt was used to measure the current absorbed by the foil, and a Dolezalek type electrometer with a sensitivity of about 800 divisions per volt to measure the emergent current. The steady deflection method with a high resistance electrometer shunt was used for some of the readings taken, but for most, the method of timing the electrometer needle motion between two fixed deflections was employed.

#### PROCEDURE

The tube was thoroughly evacuated and the tungsten filament glowed for several hours to drive off gases and to bake out the receiving chamber, which during this process was about 5 mm from the filament. After this the McLeod gauge could no longer be read and the pressure was estimated to be less than  $10^{-5}$  cm of mercury. The foil was then faced toward the filament and bombarded with 2000 volt electrons for about one-half an hour, the filament current being reduced to such a value, found by trial, as would not burn a hole in the foil. After preparation of the foil in this way, entirely reproducible results could be obtained.

#### EMERGENT VELOCITIES OF SECONDARY ELECTRONS

To determine the velocity of the emergent electrons normal to the foil when the foil was bombarded with electrons which had fallen through a definite constant potential, the emergent electrons were made to travel against a known retarding field. The receiving plate was placed about one millimeter from the foil and was large compared with this separation, therefore in a zero retarding field all but a small fraction of the emergent electrons reached the plate.

Fig. 2, for a single aluminum foil .0003 cm thick, shows the ratio of the electrometer to the galvanometer currents for an incident electron stream of constant velocity, plotted against retarding potentials applied between the receiving plate and the foil. The constant potential through which the incident electrons have fallen is indicated on the curves. The curves are alike in that they show that practically all of the transmitted electrons have velocity components perpendicular to the foil of less than 10 volts. This was checked for incident velocities up to 1545 volts; the higher velocity curves are not plotted as they are similar to the one shown for 679 volts.

It will be noticed that the current in each case reversed in sign for a retarding potential of less than 15 volts. This reversal can be accounted for in part by assuming that soft x-rays, generated by the incident electrons, traverse the foil and the retarding field (which has stopped all

or most of the emergent electrons) and liberate photo-electrons from the receiving plate. It does not seem possible, however, that the reversal for a primary velocity of 2 volts can be explained in this way. The negative current was found to be relatively small in the voltage range investigated.

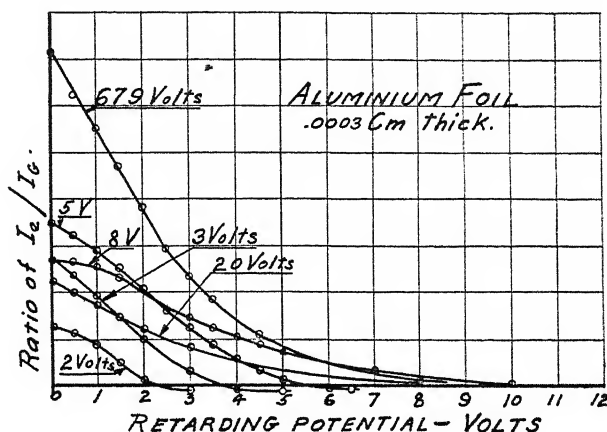


Fig. 2. Ratio of plate current to galvanometer current as a function of retarding potential, for various impact potentials.

The curves shown in Fig. 3 were constructed by differentiating graphically the curves of Fig. 2 and show, approximately, the way in which the velocities of these secondary electrons, due to the incident velocities marked on the curves, are distributed.

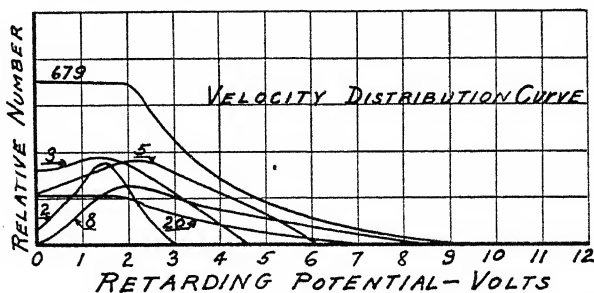


Fig. 3. Distribution of velocities of electrons reaching the plate for various impact potentials.

#### ORIGIN AND COMPOSITION OF SECONDARY CURRENT

Since the ratio of the emergent to the incident current becomes negative, in some cases for retarding potentials of only 3 volts and in all cases, regardless of the potential through which the incident electrons have fallen, for retarding potentials of 20 volts, it is clear that if the receiving

plate were made 30 volts negative with respect to the aluminum foil, a negative current would flow, made up entirely of photo-electrons from the receiving plate. On the other hand, if a positive potential of 30 volts were applied, a positive current would flow made up almost wholly of electrons coming from the aluminum foil. Some of the latter electrons, no doubt, are photo-electrons released from the foil by x-rays, but this portion should not differ greatly in number from those taking part in the negative current flow, and hence is relatively small. The greater part of the emergent current is, therefore, due to electrons liberated from the foil by some mechanism other than x-rays. Perhaps, the mean free path in aluminum for such low velocity electrons is much longer than ordinarily supposed, and the observed secondary current is due to the direct transmission of a fraction of the incident electrons. Such extraordinarily long electronic paths in the gases, argon, krypton, and xenon, were first reported by Ramsauer,<sup>4</sup> and confirmed by a number of investigators.<sup>5</sup>

Another possibility is that the electrons which take part in thermionic emission at higher temperatures, obtain a sufficient increase in velocity normal to the foil by collision with the incident electrons, to enable them to escape at room temperatures. Whatever is the mechanism by which this current is generated, to distinguish it clearly from the photo-electrons coming from the plate, it will hereafter be called "transmitted current" in this paper.

#### VARIAION WITH ACCELERATING POTENTIAL OF CURRENT TRANSMITTED THROUGH ONE FOIL

Fig. 4 shows the general dependence of the transmitted current on the accelerating potential from 0 to 1600 volts. There are two prominent maxima in these curves, the one shown at about 8.5 volts and the broad maxima at about 250 volts. The maximum shown at 8.5 volts, although always very sharp, for some unknown reason did not always appear at the same point in different trials (as for example, in the curves shown in Fig. 2). The total variation of the maximum in different runs was about 2 volts.

A large number of much smaller variations are shown in the upper curve of Fig. 4. It was thought that these maxima, or possibly the breaks between the maxima, were related to the critical potentials for aluminum reported by Horton, Andrews and Davies,<sup>6</sup> Holweck,<sup>7</sup> and

<sup>4</sup> Ramsauer, *Jahr. der Rad. und Elect.* 19, 345 (June 1923).

<sup>5</sup> Minkowski and H. Sponer, *Zeits. f. Phys.* 15, 399-409 (1923).

<sup>6</sup> Horton, Andrews and Davies, *Phil. Mag.* 46, p. 721 (1923).

<sup>7</sup> Holweck, *Ann. de Physique* 17, p. 5 (1922).

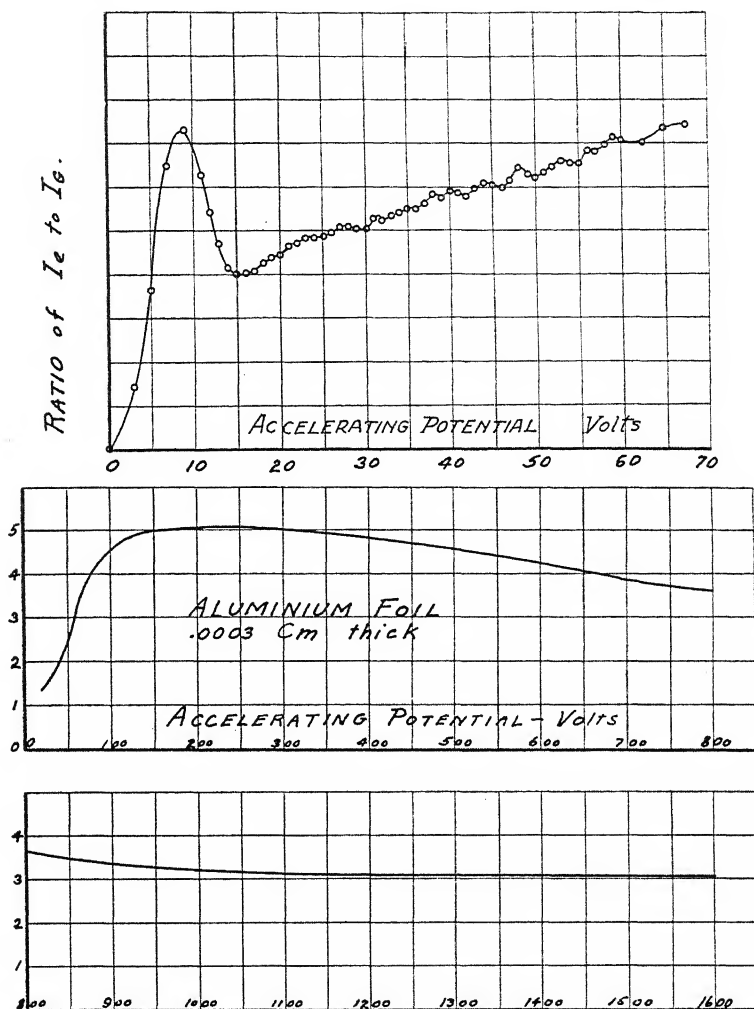


Fig. 4. Relative plate current as a function of impact potential to 1600 volts. For the two lower parts, the ordinates should be multiplied by  $1/50,000$ , approximately.

TABLE I

*Accelerating potentials of maxima*

Run 1:	41.1	41.8	42.4	43.6	44.8	45.6	46.6	48.0	48.8	49.4	51.2	
Run 2:	40.3	41.1	41.8	42.4	43.9	44.8	45.8	46.6	47.9	48.8	49.6	50.6
Run 3:	40.3	41.1		42.2	43.6	44.8	45.7	46.5	48.1	48.8	49.4	

others. Accordingly the region in the neighborhood of 40 to 50 volts was carefully examined, readings being taken at 0.2 volt intervals. Curves of the kind shown in Fig. 5 were obtained. Table I shows the potentials at which maxima were obtained in three runs taken on different days.



Maxima are tabulated rather than breaks as they are in general defined more sharply. The agreement of the values obtained in different runs is very satisfactory, especially in view of the fact that the total potential drop across the filament leads was about one volt. The maxima obtained for accelerating potentials in the neighborhood of 44 and 48 volts are especially prominent. Horton, Andrews and Davies report a critical potential at 42 volts for which they find no satisfactory explanation, and calculate a second energy level at 49.1 volts from x-ray spectra data given by Hjalmar.<sup>8</sup> No attempt was made in this investigation to correct for the initial velocity due to thermal agitation of the electrons, nor for

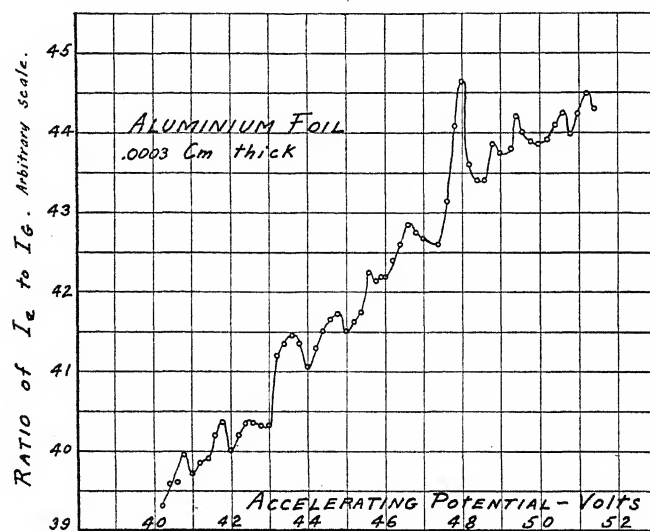


Fig. 5. Details of curve for impact potential 40 to 52 volts.

contact e.m.f., so that the figures given in Table I are accurate only relative to each other. A number of other critical potentials in the interval from 20 to 130 volts were also noticed but not carefully checked.

#### CURRENT TRANSMITTED THROUGH TWO AND THREE FOILS

Several runs were taken in which the transmission through two and three aluminum foils .0003 cm thick was measured. The transmitted current for two foils was only about 1/10,000 part of that obtained under similar conditions through one foil, but three foils cut down the current only by an additional factor of 1/10. Using two foils, small currents could be detected at about 150 volts and increased steadily with accelerat-

<sup>8</sup> Hjalmar, Phil. Mag. 41, p. 681 (1921).

ing potential. The lower curve of Fig. 6 shows the current obtained with accelerating potentials from 1190 to 1600 volts, with a positive potential of 30 volts on the receiving plate. This curve differs in two ways from the corresponding curve (Fig. 4) for the transmission through one foil, first in that the curve rises with an increase of accelerating potential while the other falls, and secondly the curve is punctuated with quite prominent breaks very similar to those obtained by Rollefson<sup>9</sup> in investigating the soft x-ray region of iron by a method in which the total photo-electric current from a plate excited by the x-rays is measured.

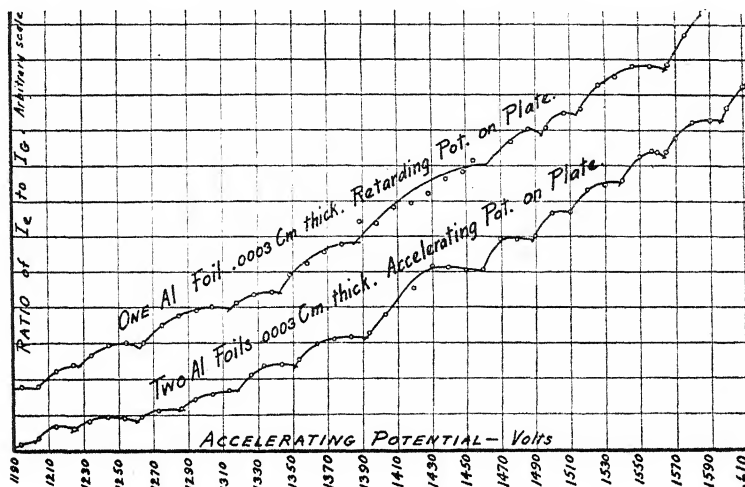


Fig. 6. Comparison of curves (1) with one foil and retarding potential on plate and (2) with two foils and accelerating potential on plate. The ordinates for the upper curve are on the average about 10 times those for the lower curve.

The current obtained under similar conditions through three aluminum foils, although only about 1/10th of that obtained with two foils, is identical in character with that shown in Fig. 6. It seemed clear then that the current being measured in the case of two and three foils was due to photo-electrons liberated from the back side of the second (or third) foil by soft x-rays generated by the incident electrons and traversing the intervening foils. To check this point a run was made using one foil, with the receiving plate maintained at a negative potential of 30 volts, so as to stop all of the electrons proceeding from the foil. By increasing the filament current, a conveniently readable electrometer current was obtained in the negative direction. The results of this run are plotted in the upper curve of Fig. 6. The two curves shown there are identical,

<sup>9</sup> Rollefson, Phys. Rev. **23**, p. 35 (1924).

except for accidental variations, and leave no doubt as to the correctness of the conclusions regarding the nature of the so-called transmitted current obtained, when using two and three foils. Incidentally, the curves of Fig. 6 yield a number of sharp breaks which appear to be critical potentials characteristic of lines in the spectrum of aluminum. The current transmitted through one foil also gives indications of feeble breaks which probably are due to that part of the current which is of photo-electric origin. In Table II are given those values, obtained from three runs each taken under different conditions, about which there appears to be no doubt.

TABLE II

One foil (neg. plate pot.)	Two foils (pos. plate pot.)	Three foils (pos. plate pot.)
1203v.	1202v.	1203v.
1225	1224	....
1265	1260	....
1315	1316	....
1342	1350	1346
(K $\alpha$ )1494	1488	....
1514	1510	....
(K $\beta$ )1566	1565	1555
	1596	1605
	1640	1640

While no attempt was made to fix the position of the breaks exactly, the results as noted in the table are in fair agreement with results published by others. Thus Holweck<sup>7</sup> gives as the K absorption discontinuity the value  $1555 \pm 10$  volts; Sommerfeld<sup>10</sup> gives the wave-lengths of the K $\alpha$  and K $\beta$  lines for aluminum, which when reduced to volts by the quantum relation become 1482 volts for K $\alpha$ , and 1551 volts for K $\beta$ . (See also Hjalmer.<sup>8</sup>) However, the author does not wish to stress the matter of critical potentials unduly, but merely to indicate here that the method employed in this investigation is capable of yielding information on this point for any metal that can be obtained in sufficiently thin sheets. Indeed, by sputtering a film of metal on the surface of some suitably thin sheet, such as aluminum, the method could probably be used to obtain information as to the critical potentials of any substance that can be sputtered.

#### POSSIBILITY OF HOLES THROUGH THE FOIL

In the opinion of the author the transmission observed is not due to holes in the foil. Neither the velocity distribution nor the variation in transmitted current with accelerating potential is such as holes would give.

<sup>10</sup> Sommerfeld, *Atombau und Spectrallinien*, 3rd edition.

In conclusion I wish to thank Professor John T. Tate, who proposed this problem, for his helpful suggestions and encouragement.

PHYSICAL LABORATORIES,  
UNIVERSITY OF MINNESOTA.  
July 2, 1924.\*

\* Received February 18, 1925—Ed.

# A RELATION BETWEEN THE CRITICAL POTENTIALS AND THE INDICES OF REFRACTION OF ELEMENTS AND COMPOUNDS

BY BERGEN DAVIS

## ABSTRACT

Quantitative applications of Lorentz dispersion formula.—(1) *Calculation of critical resonance frequencies of elements.* The Lorentz dispersion formula involves critical resonance frequencies. In the case of hydrogen, the observed value of the index of refraction  $n$  is obtained if the critical resonance potential is assumed to be 16.4 volts. This value is close to the observed ionization potential. In the cases of Zn, Cd and Hg the observed values of  $n$  are obtained if, taking into account the critical potentials of the next inner levels, the following critical resonance potentials for the outer levels are assumed, namely 4.77, 4.38 and 5.21 volts, respectively. These values lie in each case between values corresponding to two strong absorption lines. For other gases the observed and assumed potentials are as follows:

	carbon	nitrogen	oxygen	sulfur	chlorine	bromine	iodine
observed:	11.5,35	17,29.9	15.5,52	12.2,35	13.2,46	11.3,32.6	10,21
assumed:	15,35	17,29.9	18.5,52	12.2,16.2	13.2,35.3	11.3,25.8	10,13.8

The values assumed for the L<sub>III</sub> levels of carbon and oxygen agree better with the observed value for nitrogen than do the accepted values, when plotted on a Moseley diagram. However, in the case of He, Ne and A, the observed potentials do not give the observed indices, if any reasonable distribution of electrons is assumed. (2) *Calculation of index of refraction of compounds, allowing for heat of formation.* The assumption is made that the heat of formation is associated with an equal change of energy of the valence electrons. Thus in the case of water and ice, if the heats of formation are added to the critical potentials of hydrogen, the calculated values of  $n$  agree within 1/2 percent with the observed. Also in the case of diamond a good agreement is obtained only if the heat of formation is included. Data are given for other liquid and gaseous compounds and for liquid carbon and halogen compounds which tend to support this relation.—G. S. F.

THE various dispersion formulas that have been proposed contain in addition to one or more constants, terms involving possible natural resonance frequencies in the atoms of the refracting substance.

The recent advances following the success of the Bohr atomic hypothesis have led to the specifications of these natural frequencies, and experiment has determined such frequencies in some cases with a considerable degree of accuracy. In particular, the critical x-ray frequencies have been measured with great precision, and recent experiments on the refraction of x-rays in crystals<sup>1</sup> indicate that the Lorentz dispersion formula represents this refraction with some accuracy.

<sup>1</sup> Bergen Davis and R. Von Nardroff, Nat. Acad. Sci. Proc., 10, No. 2 (Feb. 1924), also 10, No. 9 (Sept. 1924).

R. Von Nardroff, Phys. Rev. 24, 143 (Aug. 1924).

C. C. Hatley, Phys. Rev. 24, 486 (Nov. 1924).

The following is an attempt to apply this formula to the calculations of the refractive indices of elements and compounds for visible light. The critical potentials and frequencies of many of the elements have now been measured and make a quantitative application of a dispersion formula possible. The calculations that follow are for sodium D ( $\lambda = 5890$ ).

The dispersion formula of Lorentz is here applied to the calculation of the indices of a number of elements in the gas form, also of a number of compounds in the gas and liquid forms. The solid form is considered in two cases, solid carbon (diamond) and solid water (ice).

The Lorentz dispersion formula for liquids and solids may be conveniently used in the form

$$\frac{n^2 - 1}{n^2 + 2} = \frac{e^2}{3\pi m} \left( \frac{N_1}{\nu_1^2 - \nu^2} + \frac{N_2}{\nu_2^2 - \nu^2} + \dots \right).$$

For application to gases where  $n$  is near unity, a convenient form is

$$\delta = - \frac{e^2}{2\pi m} \left( \frac{N_1}{\nu_1^2 - \nu^2} + \frac{N_2}{\nu_2^2 - \nu^2} + \dots \right).$$

where the index  $n = 1 - \delta$ , and  $N_1$ ,  $N_2$ , etc., are the number of electrons per unit volume having frequencies  $\nu_1$ ,  $\nu_2$ , etc.

#### REFRACTION OF ELEMENTS (GAS FORM)

In making the calculation of indices given in Table I, the plan has been adopted of seeking by trial the value of the critical potential that will give the observed index and then comparing this with the critical potential as observed. The column of the Table designated "Assumed" contains the critical potentials actually used in the calculations. These are to be compared with the observed values as given in the preceding column.

The assumed distribution of electrons in the various levels follows the scheme of Bohr, except in the case of carbon, in which case the distribution is that recently proposed by Dauvillier<sup>2</sup> and by Stoner.<sup>2</sup>

#### HYDROGEN

The critical frequency that applies in the case of x-ray refraction is that corresponding to an ionization potential. In the case of hydrogen, the value of the critical potential that would give the proper index of

<sup>2</sup> Dauvillier, *Comptes Rendus*, **179**, p. 476 (1924);

Stoner, *Phil. Mag.* (Oct. 1924).

refraction was found to be 16.4 volts. Two observed values are given<sup>3</sup> for the ionization potential of the hydrogen molecule (16 and 16.9 volts). The necessary value (16.4 volts) is quite near the most probable observed value (Table I). This happy agreement led me to extend the matter further.

TABLE I

*Elements (gas form)*

	Z	Outer levels (observed)†	Critical potentials Outer levels (assumed)	Next inner levels†	<i>n</i> (calc. and obs.)
Hydrogen	1	16 16.9	16.4	.....	1.00039
Zinc	30	(1) 4.18 (R) (1) 5.65 (R)	4.77	(6) 200 (6) 110 (6) 40	1.00206
Cadmium	48	(1) 3.95 (R) (1) 5.35 (R)	4.38	(6) 116 (6) 68 (6) 27	1.00266
Mercury	80	(1) 4.86 (R) (1) 6.67 (R)	5.21	(6) 138 (6) 92 (6) 16	1.00186
Carbon	6	(2) 11.5 (2) 35.*	(2) 15. (2) 35.	(2) 290	.....
Nitrogen	7	(1) 17. (4) 29.9	(1) 17. (4) 29.9	(2) 400	1.0003
Oxygen	8	(2) 15.5 (4) 52.*	(2) 18.5 (4) 52.	(2) 490	1.00027
Sulfur	16	(2) 12.2 (4) 35.*	(2) 12.2 (4) 16.2	(4) 150 (4) 190	1.0011?
Chlorine	17	(3) 13.2 (4) 46.*	(3) 13.2 (4) 35.3	(4) 190 (4) 272	1.00077
Bromine	35	(3) 11.3 (4) 32.6*	(3) 11.3 (4) 25.8	(6) 183 (6) 218 (6) 432	1.00113
Iodine	53	(3) 10. (4) 21*	(3) 10. (4) 13.8	(6) 63 (6) 147 (6) 217	1.00196

\* Extrapolated x-ray levels.

† Numbers in parenthesis give number of electrons in the level being considered, outer or next inner.

<sup>3</sup> Most of the data on ionization and spectra are taken from Origin of Spectra by Foote and Mohler, and from Bulletin of Nat. Research Council on Critical Potentials by Compton and Mohler. The physical-chemical data on indices, densities, heats of formation, are taken from Landolt and Bernstein and from "Thermo-Chemistry" by Thomsen.



*Elements of the second group.* These elements have two strong emission lines, the  $1S-2p_2$  and  $1S-2P$ . The potentials corresponding to frequencies of these two emission lines are known as the resonance potentials. These frequencies are also marked absorption frequencies. Taking mercury as an example, the 4.86 and 6.67 potentials are those of strong absorption frequencies. The critical frequencies of the dispersion formula are resonance frequencies. This indicates that the observed absorption is one of resonance. It will be seen in the table that the necessary critical potential in every case lies between the two observed resonance frequencies. I believe nothing is known as to the relative intensities of the absorption of these two frequencies.

*Elements of the fifth, sixth and seventh groups.* The indices are calculated in the manner previously described and are given in Table I. The distribution of the outer electrons in the sub-groups are made according to the scheme proposed by Bohr. It is quite possible that some other distribution such as suggested by Stoner might work better in some cases.

The observed (so far) critical potentials and the values that it was necessary to assume are given in adjoining columns in the table. The observed values for nitrogen apply without modification. In case of oxygen it was necessary to assume that two of the outer electrons had a critical potential of 18.5 volts and not 15.5 as apparently observed. This value, 15.5 volts, cannot be correct, however, if 17 volts is correct for nitrogen. The regular Moseley diagram for the  $L_{III}$  levels must give oxygen a higher value than nitrogen (see Fig. 14, Bulletin Nat. Research Council, Critical Potentials, Compton and Mohler). That is, oxygen must be greater than 17 volts, or if the oxygen value (15.5) is correct, then nitrogen must be less than 15.5 volts.

The critical potentials of the  $M_I$  levels of the sulfur and chlorine have not been observed, but a straight line interpolation between the values for atomic number 13 and the higher atomic numbers gives the critical potentials of these levels used in the calculations.

#### REFRACTION IN COMPOUNDS

The Lorentz dispersion formula may also be applied to the refractivity of compounds. It is found that the same values of the critical potentials that give the proper indices for the elements also give the indices very well for the compounds of these elements. That is, refractivity is an additive property provided that allowance be made for the energy involved in the heat of formation.

*Heat of formation.* The natural frequency of an outer (valence) electron is in general not the same in a compound as in an element. When elements combine to form compounds energy (heat) is either given out or absorbed. This change in the heat energy must arise from a change in the energy of the atoms involved in the chemical process. In calculating the refractivity of compounds it is assumed that this change of energy is confined to the outer (valence) electrons of the atoms. When heat is given out in combination it is assumed that this arises from a decrease in the energy of the outer electrons of one of the combining elements. This will be made clear by an example. In the case of refraction in water vapor, given in Table II, the reasonable assumption is made that only the hydrogen electrons are affected by the process of formation. The heat given out

TABLE II  
*Compounds (gas form)*

Compound	Symbol	Heat of formation	$n$ (calc.)	$n$ (obs.)
Water vapor	H <sub>2</sub> O	58	1.000254	1.000255
Hydrochloric acid	HCl	22	1.000454	1.000447
Ammonia	NH <sub>3</sub>	12	1.000355	1.000379
Nitrous oxide	N <sub>2</sub> O	-20.6	1.00044	1.00052
Nitric oxide	NO	-21.6	1.000288	1.00028
Carbon monoxide	CO	29	1.000336	1.000335
Carbon dioxide	CO <sub>2</sub>	96.5	1.00045	1.00045
Methane	CH <sub>4</sub>	20.	1.00045	1.00044
Ethane	C <sub>2</sub> H <sub>6</sub>	25	1.00077	1.00075
Ethylene	C <sub>2</sub> H <sub>4</sub>	-14.6	1.000654	1.000657
Acetylene	C <sub>2</sub> H <sub>2</sub>	-54	1.00056	1.00056

arises from a change in energy of the hydrogen electrons. The heat of formation of water vapor is 58 kg cal. per mol. This energy is equivalent to 1.28 volts change in energy for each hydrogen electron. The critical frequency of the hydrogen electrons used in this calculation is that corresponding to  $16.4 + 1.28 = 17.68$  volts. This frequency, when introduced into the dispersion formula, gives the observed index of refraction of water vapor quite accurately. This assumption that the heat of formation of compounds is related to a change in frequency of the active electrons is in line with a theory of chemical affinity just proposed by Wilsdon.<sup>4</sup> This paper of Wilsdon's marks a great advance in that it points to an explanation of chemical affinity in terms of the Bohr atom. As an illustration: Wilsdon expresses the heat of formation of the hydrogen

<sup>4</sup> Wilsdon, Phil. Mag., (Feb. 1925).

molecule from the atoms in terms of the atomic energy (in volts) as follows:

$$E = \frac{13.54}{3} \left( \frac{1}{1^2} - \frac{1}{2^2} \right) = 3.38 \text{ volts.}$$

This added to the ionization potential of the atom (13.54) should give that of the molecule:  $13.54 + 3.38 = 16.9$  volts. This is quite near the most probable value.

It may not be completely true that the whole of the energy of chemical affinity arises from the energy of the electrons only. The nuclear field may be involved. This is referred to by Wilsdon as the "trunk effect." It is probably relatively quite small.

The use that is made here of the energy of the heat of formation automatically compensates for the energy that is required to separate a diatomic molecule into single atoms for those compounds in which the atom occurs singly, for example, the formation of HCl from  $H_2$  and  $Cl_2$ . The observed heat of formation is 22 kg cal. per mol. Had it been formed from monatomic hydrogen it would have been greater by an amount equivalent to the heat of association of  $H + H$  to  $H_2$ . In that case this greater energy expressed in volts would have been added to the energy of the hydrogen atom (13.54 volts) and not to 16.4 volts as was actually done. The same is true of the chlorine. The assumption made here is that the energy change involves only changes in energy of the electrons and does not involve actions between the nuclei of the combining atoms. This principle is extended to the case of the formation of diamond by the union of similar atoms of carbon.

*Carbon.* It was desired to calculate the indices of some of the many carbon compounds. For this purpose the electrons were distributed in the two L levels in accordance with the recent suggestion of Stoner.<sup>5</sup> The values assigned are given in Table I. It was necessary to assign a critical potential of 15 volts to the  $L_{III}$  level and not 11.5 volts as apparently observed. This change corresponds to a similar one for oxygen, and makes the critical potentials of carbon, nitrogen and oxygen lie on a straight line in the Moseley diagram. The values apparently observed for these elements give a very irregular curve in the Moseley diagram and consequently cannot all be correct.

The values of the critical potentials given in Table I are those used in calculating the indices of the various compounds containing carbon that are listed in the following tables. In the case of the carbon compounds of the type  $C_nH_m$ , the energy of the heat of formation was added

<sup>5</sup> Stoner, Phil. Mag. (Oct. 1924).

TABLE III  
Elements and compounds (liquid and solid)

	Symbol	Density $\rho$	Heat of formation	Heat of evaporation	$\frac{n^2-1}{n^2+2}$	$n$ (calc.)	$n$ (obs.)	Without heat
Chlorine	Cl <sub>2</sub>	1.33	.....	2	.2180	1.357	1.367	1.358
Bromine	Br <sub>2</sub>	3.12	.....	3.64	.3300	1.57	1.66	1.585
Nitrous oxide	N <sub>2</sub> O	.870	-18	2.6	.1310	1.205	1.193	1.20
Nitric acid	HNO <sub>3</sub>	1.515	41.6	7.25	.2222	1.363	1.397	1.37
Hyd. peroxide	H <sub>2</sub> O <sub>2</sub>	1.434	46.84	.....	.2480	1.410	1.406	1.43
Water	H <sub>2</sub> O	1.00	58.	11	.2090	1.338	1.333	1.372
Ice	H <sub>2</sub> O	.917	58	12.44	.1940	1.314	1.308	1.336
Diamond	C	3.51	250	.....	.6265	2.47	2.417	3.74
			262	.....	.6200	2.44		
<i>Carbon compounds</i>								
Ethyl alcohol	C <sub>2</sub> H <sub>5</sub> OH	.798	58.47	10.8	.2290	1.37	1.362	
Methyl alcohol	CH <sub>3</sub> OH	.800	51.45	9.00	.2168	1.35	1.33	
Acetic acid	C <sub>2</sub> H <sub>4</sub> O <sub>2</sub>	1.05	105	5.6	.2312	1.38	1.372	
Ethylene oxide	C <sub>2</sub> H <sub>4</sub> O	.78	18	6.00	.2062	1.33	1.33	
<i>n</i> -butyl alcohol	(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> O	.81	70	6.6	.2513	1.42	1.40	
Benzene	C <sub>6</sub> H <sub>6</sub>	.879	-12.5	7.5	.2720	1.46	1.50	
Pentane	C <sub>5</sub> H <sub>12</sub>	.675	47.85	5.50	.2340	1.38	1.36	
Hexane	C <sub>6</sub> H <sub>14</sub>	.664	61	7.6	.2380	1.39	1.378	
Decane	C <sub>10</sub> H <sub>22</sub>	.728	-18	8.6	.2720	1.46	1.411	
<i>Halogen compounds</i>								
Hydrochloric acid	HCl	.85	22	3.6	.1570	1.25	1.252	
Chloroform	CHCl <sub>3</sub>	1.49	24.1	8.00	.2625	1.44	1.446	
Ethyl chloride	C <sub>2</sub> H <sub>5</sub> Cl	.938	30.7	6.5	.2383	1.39	1.415	
Carbon tetrachloride	CCl <sub>4</sub>	1.6	21.	8.	.2695	1.45	1.47	
Ethylene perchloride	C <sub>2</sub> Cl <sub>4</sub>	1.623	6.	.....	.2850	1.48	1.505	
Bromoform	CHBr <sub>3</sub>	2.819	14.	.....	.3330	1.58	1.589	
Ethyl bromide	C <sub>2</sub> H <sub>5</sub> Br	1.455	23.	6.6	.2548	1.42	1.424	
Hydrogen bromide	HBr	1.63	12.26	4.18	.1915	1.31	1.325	
Methyl iodide	CH <sub>3</sub> I	2.258	8.00	6.54	.3230	1.56	1.53	
Ethyl iodide	C <sub>2</sub> H <sub>5</sub> I	1.93	11.00	7.00	.3100	1.53	1.515	
<i>Sulfur compounds</i>								
Hydrogen sulfide	H <sub>2</sub> S	.....	2.75	.....	.....	1.00071	1.00062	
Carbon disulfide	CS <sub>2</sub>	.....	-26	.....	.....	1.00132	1.00147	
Sulfur dioxide	SO <sub>2</sub>	.....	71	.....	.....	1.00080	1.00068	
Sulfur trioxide	SO <sub>3</sub>	.....	92	.....	.....	1.00092	1.00074	
Carbon disulfide	CS <sub>2</sub>	1.263	-26	6.8	.3330	1.58	1.62	
Sulfur dioxide	SO <sub>2</sub>	1.377	71	5.8	.2595	1.43	1.41	
Sulfuric acid	H <sub>2</sub> SO <sub>4</sub>	1.827	193	.....	.3230	1.56	1.43	

to the hydrogen electrons only. This was done to be consistent with the scheme used in the formation of water. It is probably not correct, as there is undoubtedly a bond between the carbon atoms themselves. The relative strengths of the carbon and hydrogen bonds are not known. However, a change in the distribution of heat energy from the hydrogen to the carbon atom would not affect the final result appreciably, as their critical potentials are nearly the same (15 and 16.4 volts). Also, the heats of formation of most carbon compounds are small and so do not affect the indices very greatly.

*Diamond.* The same critical potentials of carbon that apply so well in the case of carbon compounds also give a good value for the index of refraction of diamond. In order to calculate this index it is necessary to know the heat of formation of diamond. This is an important matter in the case of diamond, as the heat of formation appears to be very large. This heat of formation has recently been calculated by Landé,<sup>6</sup> making use of its known structure and of some recent measurements of its compressibility. Two values of the heat of formation of diamond are given by Landé, 250 and 262 kg cal. per mol. The crystal structure of diamond as determined by Bragg shows that each carbon atom makes four points of contact with neighboring atoms. The energy of the heat of formation was consequently divided between the four electrons of the carbon atom. The heat of formation, 262 kg cal., gives a change in energy of 2.88 volts for each carbon electron. This, added to the critical potentials (15 and 35 volts), gives 17.88 and 37.88 volts respectively, as the critical potentials of these carbon electrons in diamond. These give a very good value for the calculated index (2.44) as shown in the table. On the other hand, if the heat of formation is not included, the calculated index is 3.74. This is far greater than the observed value (2.417).

The total heat of formation of compounds to the liquid state was divided into two parts, that of the formation of the compound to a gaseous state (chemical process) and the heat of evaporation (a physical process). The heat of evaporation was distributed among all the outer ring electrons of all the atoms involved. To illustrate in the case of water and ice, the heat of formation, 58 kg cal., was added to the critical potential of the hydrogen electrons, but the additional energy of condensation to the form of water (11 kg cal.) and to the form of ice (12.44 kg cal.) was added to the critical potentials of both the hydrogen and oxygen electrons. In most cases the heats of evaporation were so small that this correction was not important. The last column of Table III contains

<sup>6</sup> Landé, *Zeits. f. Phys.* 4, 410, also 6, 10 (1921).

value of the indices in a few cases which are calculated from the critical potentials alone without allowing for the heats of formation and evaporation.

#### DISCUSSION

The foregoing gives a physical basis for the molecular refractivity of compounds so well known to the organic chemist. It also explains the atomic additive property of refractivity. In the case of hydrogen the critical potential made use of is an ionization potential. The frequency that applies in the Lorentz dispersion formula is a resonance (absorption) frequency. This would indicate that unexcited molecular hydrogen should have an absorption band at  $\lambda = 760$ .

The critical potentials for the subgroup of four electrons in the case of sulfur and chlorine have not been observed. As shown by Table III the scheme of critical potentials does not give the observed refractive indices of sulfur compounds very well. The values of the critical potentials that give the proper value for the observed index of sulfur vapor are not proper for the compounds. This is an apparent deviation from the atomic additive property of refractivity. It is not impossible that the observed index of refraction for sulfur vapor is in error. Sulfur vaporizes at a rather high temperature, and is a mixture of  $S_2$ ,  $S_4$ ,  $S_6$ ,  $S_8$ . Error is possible in reducing observations to equivalent values of  $S_2$  at zero. The last column of Table I also suggests that the observed index for sulfur may be in error. The refractivity tends to increase regularly with the atomic number of the elements, but the value for sulfur is much too large for this regular law.

*The rare gases.* The scheme of critical potentials will not give the observed indices for helium, neon and argon. It is a failure unless the electrons in the outer levels have a distribution in subgroups quite different from what is now believed to be the case.

PHEONIX PHYSICAL LABORATORIES,  
COLUMBIA UNIVERSITY,  
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## ON THE KINETIC THEORY OF THE THERMIONIC EFFECT

By N. P. RASHEVSKY

## ABSTRACT

Making different assumptions as to the behavior of electrons inside a solid body, statistical deductions for the thermionic currents in the corresponding cases are made. All the formulas obtained are of the type  $i = AT^a e^{-b/T}$  and differ only in the values of  $A$  and  $a$ . The following cases are investigated. (1) The electrons inside a body are assumed to behave like a perfect gas. In this case  $a$  comes out  $1/2$ . (2) The electrons are assumed to be arranged in a space-lattice with the same dynamical properties as the ordinary crystal-lattices. For this case  $a = -1$ . (3a) All electrons are assumed to be moving on quantized orbits with the same quantum number and energy. For this case  $a = 2$ . The case (3b) in which the electrons inside the metal are assumed to be divided into  $S$  groups, each group  $i$  moving in an orbit with the quantum number  $i$ , is more complicated and will be discussed in a separate paper. The experimental results are at present not accurate enough to decide between these values of  $a$ .

I. The problem of emission of electrons from hot bodies is usually regarded as a problem of evaporation. Therefore thermodynamic considerations applied to the thermionic effect lead to expressions similar to those applied to evaporation.

The thermodynamic expression for the vapor-pressure<sup>1</sup> is

$$p = \text{const. } T^{-(c-c_p)/R} e^{-\lambda/T} \quad (1)$$

$\lambda$  being a constant (the heat of evaporation),  $c$  the heat capacity of the solid,  $c_p$  the heat capacity of the vapor at constant pressure, and  $R$  the gas constant.

At this point the pure thermodynamic method is exhausted. Without making further hypotheses as to the connection between  $c$ ,  $c_p$  and  $R$ , hypotheses which are more of a kinetic character than thermodynamic, we are unable to determine the power of  $T$  in (1). For monatomic gases we have  $c_p = (5/2)R$ , and assuming the validity for the solid of the law of Dulong and Petit we have  $c = 3R$ . Then (1) reduces to

$$p = \text{const. } \times T^{-1} e^{-\lambda/T}.$$

The effect of different kinetic assumptions on the final result is explicitly seen in different *kinetic* deductions of the vapor-pressure formulas; due to this difference of assumptions involved, P. Ehrenfest and V. Trkal,<sup>2</sup>

<sup>1</sup> W. Nernst, Theoretical Chemistry, 10th German ed., trans. by N. Godd, p. 68 (1923).

<sup>2</sup> Ehrenfest and Trkal, Amst. Proc. 23, p. 182 (1920).



D. Enskog<sup>3</sup> and R. H. Fowler<sup>4</sup> arrived at different values of the power of  $T$ , although all their formulas are of the same type as (1).

The formulas for the number of electrons emitted by a hot body also vary according to the assumptions involved.

The purpose of the present investigation is to deduce on a purely kinetic basis formulas for the thermionic current, under different special assumptions as to the behavior of electrons inside the metal. All the formulas will be of the type

$$i = A T^a e^{-b/T} \quad (2)$$

the exponent  $a$  depending on the assumptions involved.

Even without any kinetic investigation, by pure thermodynamic reasoning we may find the physical meaning of the hypothesis which leads to  $a=2$ . Formula (1) may be applied to the electrons outside the metal. Remembering now that  $p$  is connected with  $n_0$  by the expression

$$p = n_0 k T \quad (3)$$

and  $n_0$  is connected with  $i$  by

$$i = n_0 e \sqrt{kT/2\pi m},$$

we see that to a power  $d$  of  $T$  in (1) corresponds a power of  $T$  equal to  $d - \frac{1}{2}$  in (2). To obtain therefore  $a=2$  in (2) we must have

$$(c - c_p)/R = 5/2. \quad (4)$$

Now there can be little doubt that if it is admissible to consider the outside electrons as a perfect gas, we must consider it as a monatomic one, so that we have in any case

$$c_p = (5/2)R. \quad (5)$$

It follows immediately, then, that (4) may be obtained only by putting  $c=0$ , that is by assuming the energy of the internal electrons to be zero, or at least independent of the temperature. This assumption in slightly different forms is made by both S. Dushman and S. Roy.<sup>5</sup>

In any other case we will obtain values for  $a$  different from 2; and as it is evident that the assumption  $c=0$  is only a more or less close approximation, we see at once that  $a=2$  is also only an approximation.

II. We now proceed to the investigation of different possible typical assumptions as to the electrons inside the metal.

These may be of the three following kinds:

(1) The electrons inside the metal are free and behave like an ideal gas. Their energy is only kinetic.

<sup>3</sup> Enskog, Ann. der Phys. 72, 321 (1923).

<sup>4</sup> Fowler, Phil. Mag. p. 30 (1923); on p. 31 is given a comparison of different formulas.

<sup>5</sup> Dushman, Phys. Rev. 21, 623 (1923); Roy, Phil. Mag. 47, 561 (1924).

(2) The electrons are bound, and form a space-lattice, like the positive ions, and are held in their equilibrium positions by quasi-elastic forces, the displacements being small.

(3) The electrons are bound, but do not form a space lattice. They move on quantized orbits. The orbit of an electron may belong either to a single positive ion, or to the crystal<sup>6</sup> as a whole. As J. Frenkel points out, this second possibility is the *most probable from the point of view of electrodynamics*.

In all three cases it is assumed that outside the hot body the electrons behave like a perfect gas. As to the statistical methods of treating our problem, we will use that employed by M. Born in his deduction of the formula for vapor-pressure.<sup>7</sup>

III. Case (1). *Electrons assumed to be free.* Suppose from  $N$  electrons, available for distribution,  $n$  are outside and  $n'$  inside the metal. Denote the work necessary to remove all  $n$  electrons from the metal by  $G = ng$ ,  $g$  being the average work per electron. Denote further by  $p_i$  ( $i = 1, 2 \dots 3n$ ) the momenta of the outside electrons; then the total energy of these electrons is

$$E_e = (1/2m) \sum_{i=1}^{i=3n} p_i^2 + ng \quad (6)$$

$m$  being the mass of an electrons.

In the same way, for the inside electrons we find

$$E_i = (1/2m) \sum_{i=1}^{i=3n'} p_i'^2 \quad (7)$$

$p_i'$  being the momenta.

The probability that the electrons 1, 2, 3, ...  $3n$  are outside while  $(n+1)$ ,  $(n+2)$ , ...  $N$  are inside the metal is

$$W' = A \int e^{-(1/kT)(E_e + E_i)} dq_1 \dots d p_{3n} dq'_1 \dots d p'_{3n'}, \quad (8)$$

$q_i$  and  $q_i'$  being the coordinates of the outside, and inside electrons respectively. The integration over these variables is to be taken over all the outside volume  $V$  and all the inside volume  $V'$  of the metal, respectively. The integration over  $p_i$  and  $p_i'$  is to be taken from  $-\infty$  to  $+\infty$ . This gives

$$W' = A e^{-ng/kT} V^n V'^{n'} (2\pi m kT)^{3N/2}. \quad (9)$$

<sup>6</sup> J. Frenkel, Zeits. f. Phys. 29, 214 (1924).

<sup>7</sup> M. Born, Atomtheorie des festen Zustandes, Encykl. der Math. Wiss., Band V, Heft 4, p. 705.

To obtain the probability that any  $n$  electrons are outside and any  $n'$  inside the metal, we have to multiply  $W'$  by  $N!/n!n'!$ . This gives

$$W = A(N!/n!n'!)e^{-n\phi/kT}V^nV'^{n'}(2\pi mkT)^{3N/2}. \quad (10)$$

The equilibrium state is defined by the maximum of  $\log W$ . Using Stirling's formula,  $\log n! = n \log n - n$ , and putting  $d \log W/dn = 0$ , we find

$$\log n = -g/kT + \log(N-n) + \log V/V' \quad (11)$$

or

$$n(N-n) = (V/V')e^{-g/kT}. \quad (12)$$

We introduce now the concentration  $n_0 = n/V$  of the outside electrons and  $n'_0 = n'/V'$  of the inside ones.  $n'_0$  may be considered as constant because  $n' = N - n$  is approximately equal to  $N$ ;  $N$  being about  $10^{10}$  larger than  $n$ .<sup>8</sup> We obtain

$$n_0 = n'_0 e^{-g/kT}, \quad (13)$$

and for the thermionic current we obtain finally the expression

$$i = \sqrt{k\epsilon^2 n'_0 / 2\pi m} T^{3/2} e^{-g/kT} \quad (14)$$

IV. *Case 2. Electrons assumed bound in a space-lattice.* The  $n$  electrons arranged in a space-lattice perform vibrations with  $3n'$  frequencies  $\nu_i$  ( $i = 1, 2, \dots, 3n'$ ). Their potential energy is in general a function of the coordinates of all electrons and ions in the space-lattice, but by the introduction of normal coordinates<sup>9</sup> it can be brought to the form

$$\frac{1}{2} \sum_{i=1}^{i=3n'} \omega_i^2 q_i'^2, \quad (15)$$

while if  $p_i'$  are the momenta corresponding to the normal coordinates  $q_i'$ , the kinetic energy is equal to

$$\frac{1}{2} \sum_{i=1}^{i=3n'} p_i'^2. \quad (16)$$

We have therefore,

$$E_i = \frac{1}{2} \sum_{i=1}^{i=3n'} (p_i'^2 + \omega_i^2 q_i'^2), \quad (17)$$

while the expression (6) remains for the outside electrons.

We follow now the method used by Born in the deduction of the vapor-pressure formula, and find

$$\log n = -g/kT + \log V - (3/2) \log T + (3/2) \log (2\pi\nu_0^2 m/k)$$

or

$$n_0 = (2\pi\nu_0^2 m/k)^{3/2} T^{-3/2} e^{-g/kT} \quad (18)$$

<sup>8</sup> Richardson, *Emission of Electricity from Hot Bodies*, 2nd ed. (1921) p. 40.

<sup>9</sup> M. Born. loc. cit.<sup>7</sup> p. 593.

where

$$\nu_0^{3n'} = \prod_{i=1}^{i=3n'} \nu_i. \quad (19)$$

Hence

$$i = (2\pi m \nu_0^3 e/k) T^{-1} e^{-e/kT} \quad (20)$$

V. *Case 3. Electrons assumed bound in orbits.* This may be subdivided in two sub-cases:

(a) All electrons inside the metal move on orbits with the same quantum number, i. e. with the same energy  $e$ .

(b) The  $n'$  electrons inside the metal are divided into  $s$  groups, each electron of a group  $i$  ( $i=1, 2, \dots s$ ) moving in an orbit with the quantum number  $i$  and having thus the energy  $e_i$ ; the number of electrons in the  $i$ -group is  $n_i'$ . Thus  $n' = \sum_1^s n_i'$ .

For the subcase (a) we have

$$W' = A e^{-n'e/kT} \int e^{-E_e/kT} dp_1 \dots dq_1 \dots \quad (21)$$

$E_e$  being given by (6).

Thus

$$W' = A e^{-(N-n)e/kT} e^{-n_0 e/kT} V^n (2\pi m kT)^{3n/2} \quad (22)$$

To obtain  $W$  we multiply only by  $N!/n!n'!$ , but do not need to multiply by  $n'!$  as all orbits are similar. In the case of a space-lattice formed by  $n$  electrons, two electrons chosen at random differ in general by their frequencies as there are  $3n$  frequencies for  $n$  electrons. There is thus a *physical* difference between them, while in the case of absolutely similar orbits no such difference exists. Thus we finally obtain by computing  $W$  and putting  $d \log W/dn = 0$ ,

$$\log n - \log (N-n) = \log V - (g-e)/kT + 3/2 \log (2\pi m kT)$$

or introducing again  $n_0$ , and putting  $n'$  for  $N-n$

$$n_0 = n' (2\pi m k)^{3/2} T^{3/2} e^{-(g-e)/kT} \quad (23)$$

or

$$i = 2\pi n' e m k^2 T^2 e^{-(g-e)/kT}. \quad (24)$$

The factor  $T^2$  in this case is due to the fact that we have assumed the energy  $E_i$  of the electrons in the crystal to be  $n'e$ , i. e. independent of  $T$ , and therefore we have in (1)  $c = dE/dT = 0$ .

In the subcase (b) things are much more complicated. We have

$$W' = A \prod_{i=1}^{i=s} e^{-n_i' e_i/kT} \int e^{-E_e/kT} dq_i \dots dp_i \dots \quad (25)$$

and to obtain  $W$  we must multiply  $W'$  by

$$N! / n! n_1! n_2' \dots n_s'!$$

$W$  is a function of  $n$  and of any  $(s-1)$  of the  $n_i'$  the remaining one  $n_i'$  being given by the equation

$$n + \sum_{i=1}^{i=s} n_i' = N.$$

We have the equations

$$dW/dn=0; dW/dn_1'=0; \dots dW/dn_i'=0$$

from which we find  $n$  and  $n_i'$ .

The explicit solution of the problem requires the knowledge of the function giving the energies  $e_i$  in terms of quantum numbers. We may also simplify the problem by assuming that the partition function of the inside electrons is not considerably altered by the emission, and therefore  $n_i'$  are known functions of  $e_i$  and  $T$ .

The case 3b seems to be the most plausible and will be investigated in another paper. We did not apply the quantum theory when dealing with space-lattices. This, of course, limits the application of our considerations to high temperatures, when the quantum theory degenerates into the classical one and the law of equipartition holds with greater approximation. Experimentally we nearly always use this range of temperatures.

It is noteworthy that the experimental results do not allow us up to the present time to make a choice between the different cases discussed in this paper. In a quite recent article<sup>10</sup> Dushman, Rowe, Jessie Ewald and Kidner give the results of very accurate measurements on tungsten, molybdenum and tantalum. They find that the points representing  $\log i - 2 \log T$  as a function of  $1/T$  fall very accurately on a straight line. Unfortunately, a very close agreement is obtained also in plotting  $\log i - \frac{1}{2} \log T$  (which corresponds to  $a = \frac{1}{2}$ ) or  $\log i + \log T$  (which corresponds to  $a = -1$ ). Using the values given in the Table V of the article mentioned, plots were made and it was found that no preference can be given to any of the expressions.

RESEARCH DEPARTMENT,  
WESTINGHOUSE ELECTRIC AND MANUFACTURING CO.  
EAST PITTSBURGH, PA.  
March 26, 1925.

<sup>10</sup> Dushman, Rowe, Ewald and Kidner, Phys. Rev. 25, p. 338 (1925).

## PHOTO-RESISTANCE EFFECT FOR METALS AT LOW TEMPERATURES

BY RUSSELL S. BARTLETT

## ABSTRACT

Photo-resistance effect for sputtered metallic films at low temperatures.—Waterman's equilibrium theory of resistance predicts an effect for metals, increasing as the temperature is decreased. To test this, thin sputtered films, after aging, were held at liquid air temperature and illuminated with light from a quartz mercury vapor arc, with or without screens. *Bismuth* showed the largest decrease in resistance,  $16 \times 10^{-6}$ , *palladium*  $14 \times 10^{-6}$ , *copper*  $1.6 \times 10^{-6}$ , *platinum* even less and *gold* and *silver* no detectable change. The order of these metals is in agreement with the theory. The effect was not in general instantaneous but increased with time along a saturation curve, and in the dark returned only slowly toward the original value. The effective wave-length was found to be beyond 3000Å for fresh Bi films, but the threshold seemed to move to longer wave-lengths with age. Some older Bi films showed a reverse positive effect of even larger magnitude which apparently is due to longer wave-lengths, but the exact circumstances were not definitely fixed. The magnitude of the negative effect for Bi decreased rapidly with increasing temperature, to  $3 \times 10^{-6}$  at  $-110^\circ$ . *Tellurium*, sensitive at room temperature, showed a 70 percent greater effect at  $-185^\circ\text{C}$ .

Temperature coefficient of resistance of sputtered films.—For Bi the coefficient decreased from .0014 at  $0^\circ\text{C}$  to practically zero at  $-185^\circ\text{C}$ . In general, the coefficients were smaller for the sputtered films than for the same metals in bulk.

## INTRODUCTION

IT APPEARS to be well established that metals, under the influence of light, show no change in electrical conductivity other than that due to the heating effect of the radiation absorbed.<sup>1</sup> As we pass from good conductors to the poorly conducting metalloids and non-metals, we find an increasing photo-resistance effect. Waterman<sup>2</sup> has suggested a theory which accounts for this variation and at the same time indicates that metals should show a photo-resistance effect at very low temperatures.

## THEORY

From theoretical considerations, Waterman derived an expression for the electrical resistance of the form

$$\rho = AT^a e^{b/T - cT}$$

<sup>1</sup> L. Ancel (Zeits. Elektrochemie, 9, 695, 1903) makes a reference of uncertain significance to light sensitivity of metal plates. Since, however, nothing further on the subject can be found in the scientific journals of that time, it would seem that he was merely speculating on the possibility of such an effect.

<sup>2</sup> Waterman, Phys. Rev. 22, 259, 1923.

where  $A$  is a constant characteristic of the element, and  $a$  is a constant having the value  $5/4$  for most metals. For such metals

$$b = (\phi_0 - \psi_0)/2R$$

where  $\phi_0$  is the photo-electric and  $\psi_0$  the thermionic work function;  $c$  involves the specific heat of electricity.<sup>3</sup> The effect of incident light should be to reduce  $\phi_0$  and thus diminish the energy  $(\phi_0 - \psi_0)$  necessary to create a free electron. This disturbs the equilibrium condition and leads to an increase in the number of free electrons in the metal.

If  $b$  is calculated from specific resistance data at different temperatures, it is found to be small for all metals, so that the factor  $e^{b/T}$  is nearly unity except at low temperatures. But when  $T$  is sufficiently small this factor becomes effective, and a change in  $b$ , due to incident light, should alter the resistance. Assuming, as seems reasonable, that when  $b$  is large its change under the influence of light will also be large, it is possible to predict the metals most favorable for the result sought.

Such calculations were made, indicating that Pd, Cu, Pt, Rh, in that order, are particularly suited for this work. Following them are Na, Cd, Sn, Te, Ag, Au, etc.

Bismuth is peculiar in many of its properties, and as such might not follow the simple theory outlined. But considerations similar to those applied to other metals indicate a sensitivity larger than that for palladium. Further favorable indications are found in the fact that bismuth has a high specific resistance and is a border substance between metals and non-metals.

Iron and nickel were uncertain because of transition points and the effect of impurities.

#### EXPERIMENTAL PROBLEM

*Preparation of thin films.* A preliminary trial was made with thin metallic foils and fine wires at liquid air temperature, but no change in resistance was noted under the influence of light. It appeared that thin films of a wide variety of metals were necessary, and the method of cathode sputtering was selected as the means for obtaining these. The apparatus used was similar to that described by Richtmyer and Curtiss<sup>4</sup> and by Perkins.<sup>5</sup> Au, Ag, Pt, and Pd sputtered readily in residual air with a 2 to 4 cm cathode dark space. Bi and Te required a dark space of

<sup>3</sup> This term, which is in general small except at high temperatures, has been added by Waterman in a supplementary paper: Waterman, Phys. Rev. 23, 781, 1924.

<sup>4</sup> Richtmyer and Curtiss, Phys. Rev. 15, 465 (1920).

<sup>5</sup> Perkins, Jour. de Phys. et le Radium (IV), 4, 246 (1923).



6 cm or more for most rapid deposition. For copper, to avoid oxidation, the discharge tube was filled with hydrogen at a pressure just sufficient to support the discharge at 10,000 volts.

The thickness of the films was obtained by weighing, assuming the density to be the same as that for bulk metals. The thickness, below a certain critical value, seemed to have no effect upon the results.

It was found that the resistance of freshly sputtered films varied considerably with time, so that it was necessary to age all the films either naturally or artificially before taking resistance measurements. The degree or method of this aging appeared to have no effect upon the behavior of the film under the influence of light. An exception to this in the case of bismuth is discussed later. Of all the metals used bismuth alone showed an increase of resistance with aging, the others all showing a very marked decrease.

Contacts which maintained a constant resistance over the range of temperatures investigated were made by sputtering the ends of the films heavily with gold, and attaching permanent leads by means of brass clamps. For higher resistance films, "clamping paste," furnished through the kindness of the General Electric Company, was used with similar clamps, and proved satisfactory. The connections to the resistance measuring apparatus were made by dipping the leads into mercury cups.

*Source of radiation.* As a source of radiation a quartz mercury vapor lamp was used. A quartz lens, quartz cell, and shutter were arranged as shown in Fig. 1. This gave a limit on the short wave-length side of about 2000 Å. Absorbing filters, as described by Williamson,<sup>6</sup> were used in the cell to limit further the wave-length range, to fix the region of

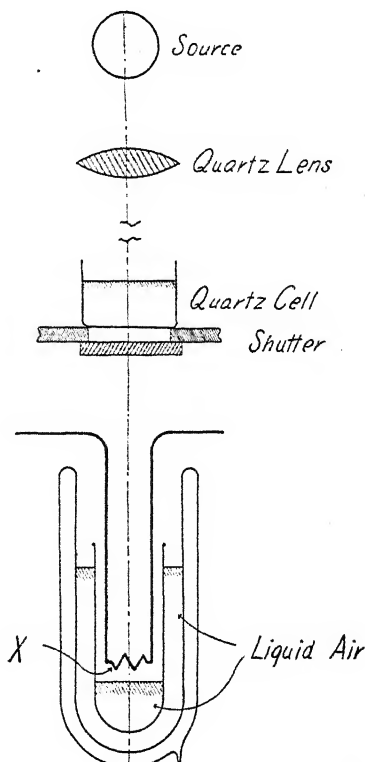


Fig. 1. General arrangement of apparatus.

<sup>6</sup> Williamson, Phys. Rev. 21, 107 (1923).

effective wave-lengths, and to eliminate as far as possible the inactive heat radiation.

*Temperature control.* The temperature of liquid air, taken as about  $-185^{\circ}\text{C}$ , was the lowest available. For this temperature the metal films were placed in actual contact with the liquid air. By means of films sputtered on quartz and inverted with the metal just touching the liquid air, the absorption of light in the liquid air was avoided, and by comparison it appeared that the absorption in a thin film was negligible. Slightly higher temperatures could be obtained with sufficient constancy by means similar to that shown in Fig. 1, the metal foil being suspended above the liquid air and surrounded by it, though not in actual contact. For still higher temperatures a bath of petroleum ether was used. Temperature measurements were made with a pentane thermometer, calibrated in liquid air and in freezing ether, acetone, chloroform, and distilled water. Sufficient time was always given before taking measurements to allow the temperature to become constant.

*Resistance measurements.* A potentiometer method was found to be the most satisfactory for measuring small changes of resistance and at the same time eliminating extraneous disturbing factors. A Leeds and Northrup type H.S. galvanometer was used in connection with a Wolff potentiometer of 15,000 ohms internal resistance. Lead storage cells furnished a constant potential difference. Since the resistance of the film was small compared to the resistance in series with it, after the bridge had been balanced and the key closed, the change in resistance on illumination could be measured by the galvanometer deflection. The current through the metal strips was kept at as large a value as possible without appreciable heating. With this arrangement it was possible to measure changes of resistance of one part in three million, or slightly better. By taking a large number of readings under identical conditions, errors due to slight fluctuations were largely eliminated. The arrangement of the apparatus was such that the flow of heat between the warm and cold parts would have a very small disturbing influence, so that after a short time a very good balance could be obtained. By measurements made on a film sputtered completely except for a slight break in the middle, it was shown that the changes in conductivity of glass and liquid air under the influence of light, were of such an order as to have no appreciable effect on the result, and that conduction due to emission electrons could be neglected.

*Elimination of temperature effects.* The most serious problem was that of distinguishing changes in resistance due to a slight rise in temperature

upon illumination from the true photo-resistance effect looked for. Careful measurements were made to determine the nature of the temperature coefficient of resistance, in sign and magnitude, and its variation with temperature. Special care was taken with bismuth and palladium because of their negative coefficients. A typical curve of the resistance temperature relation, given in Fig. 2 (A), shows that the coefficient for Bi is continuously negative down to  $-185^{\circ}\text{C}$ ,<sup>7</sup> but that the value decreases rapidly towards this limiting temperature, so that the possible effect of heating would be very small for liquid air temperature. A smaller and

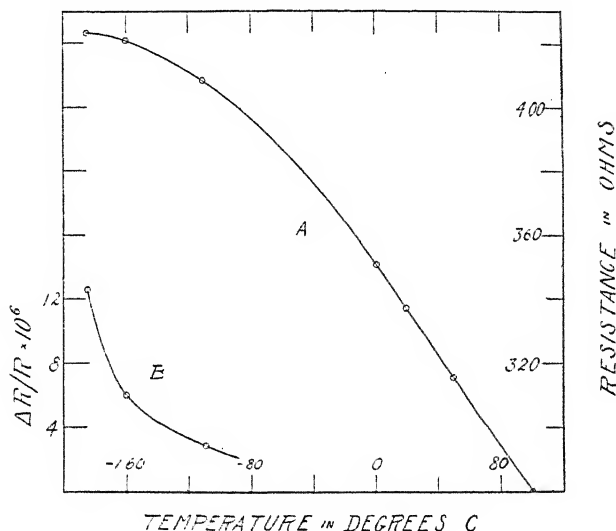


Fig. 2. Bismuth films. Curve A. Resistance as a function of temperature.  
Curve B. Photo-resistance effect as a function of temperature.

generally similar coefficient was obtained for palladium. Tellurium showed a much larger negative coefficient. The other metals used all showed positive temperature coefficients of resistance, though much smaller than for the same metals in bulk.<sup>8</sup>

From these data and from the results of investigations on screening by distilled water and on constant temperature baths, it was concluded that the effect due to heating by incident radiation was in all cases small, and entirely negligible if a distilled water screen was used. Since this

<sup>7</sup> Becker and Curtiss (Phys. Rev. **15**, 457, 1920) have remarked this negative temperature coefficient for bismuth for the range  $0^{\circ}$  to  $150^{\circ}\text{C}$ . The results check very well for the region common to both investigations.

<sup>8</sup> Longden (Phys. Rev. **11**, 40 and 80, 1900) and Patterson (Phil. Mag. **4**, 652, 1902) have both noted this low temperature coefficient of resistance for sputtered films.

screen cut off somewhat on the short wave-length side, it was thought advisable also to take some measurements without it.

### RESULTS

Sputtered films of gold and silver showed no measurable change in resistance under the influence of light. Platinum showed a probable decrease in resistance, but so small as to be barely discernible, less than one part in  $10^6$ . This appeared only for the thinnest films used, about  $10^{-6}$  cm in thickness, and for the shortest wave-lengths, below 2500 Å.

Copper showed a very definite and instantaneous decrease in resistance under the influence of light for the thinnest films used,  $1.5 \times 10^{-6}$  cm in thickness. The decrease was found to be between 1.1 and 1.6 parts in  $10^6$  for different films, the corresponding increase on darkening being about half. It is probable that the original value was reached after a slight lapse of time.

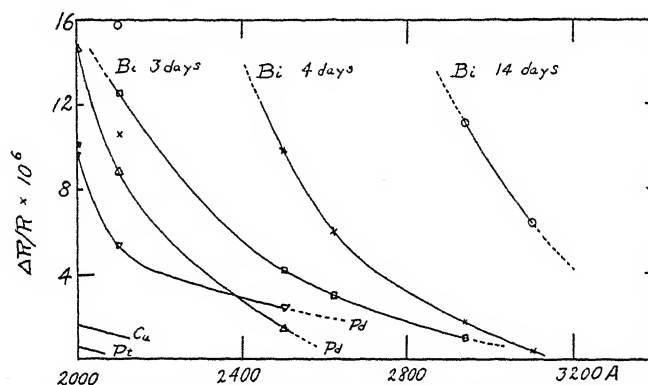


Fig. 3. Photo-resistance effect as a function of wave-length.

Palladium and bismuth showed much larger changes, amounting to 14 and 16 parts in  $10^6$  respectively. For both of these metals various absorbing screens were used, the decrease in sensitivity with longer wave-lengths being indicated in Fig. 3. For bismuth the decrease in sensitivity for increasing temperature was investigated, the results appearing in Fig. 2 (B).

It would be expected that any effect would depend directly on the intensity of incident light, and this was roughly confirmed. For the observations noted above or indicated in curves, the same intensity was used in all, excepting that the use of an absorbing screen to cut out certain wave-lengths slightly diminished the intensity of others.

Tellurium films, sensitive at room temperature, showed a considerable increase in sensitivity at liquid air temperature, in agreement with the

prediction of theory. The sensitivity decreased with increasing wavelength, the effective limit being near 4500Å at 20°C, and slightly longer at -185°C. A curve showing the decrease of resistance with time of illumination at 20°C and at -185°C is given in Fig. 4 and will prove useful for comparison with others to be discussed later.

These results conform rather well with predictions. Bismuth might be expected, from resistance data, to show the largest light sensitivity, and such was the case. Palladium, copper and platinum follow in that order, from observation, and from theoretical considerations. The evidence appears, then, to support Waterman's prediction of a light sensitivity for metals at low temperatures, and to justify the general form of his equation as far as the term  $e^{b/T}$  is concerned. Quantitative deductions are not possible with the data available at present.

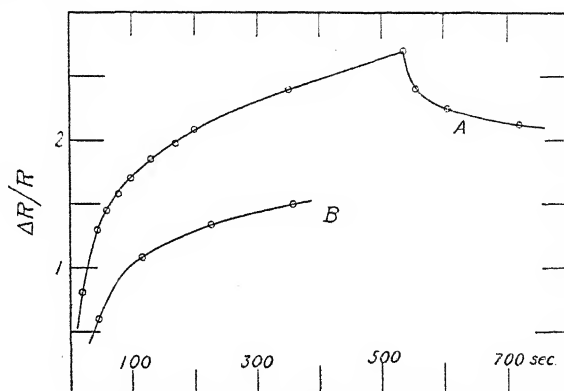


Fig. 4. Tellurium films. Photo-resistance effect as a function of time. Curve A. At -185°C; Curve B. At 20°C. Break in A is at the point where illumination was shut off.

It seems probable that the magnitude of this light sensitivity could be greatly increased through the use of thinner films, shorter wave-lengths, and lower temperatures. With sufficient refinements in these particular it should be possible to find a light sensitivity for many more metals.

In addition to the results given above, *another peculiarity of bismuth films* was noted, an *increase* of resistance under the influence of light for certain conditions. Thus a single film would at one time show a decrease in resistance and at another an increase.

A film soon after sputtering showed only the normal and expected decrease in resistance. With continued aging the reverse effect increased. At a certain time in this aging process it was possible to obtain a decrease in resistance by using a distilled water screen, and an increase without the screen. With further aging the increase of resistance alone could be

noted, though the distilled water screen always decreased this greatly. A screen of glass had a similar and somewhat greater effect, while paraffin transmitting in the long infrared did not entirely eliminate the change. It appears probable that this increase in resistance is due to long wavelengths.

The reaction to light appeared to be practically instantaneous, reaching a nearly steady value after a short time. The increase in resistance was in some cases as large as 8 parts in 10,000 or about 50 times as great

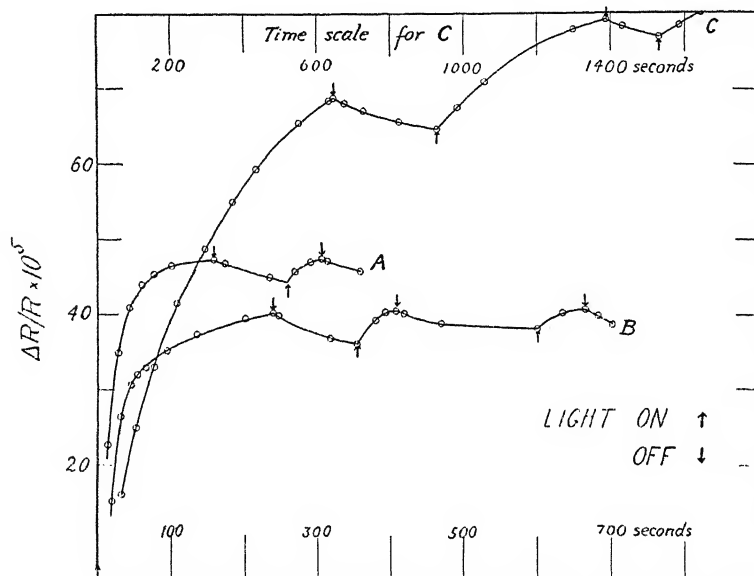


Fig. 5. Bismuth films. Negative photo-resistance effect as a function of time.

Curve A. Age 14 days, thickness  $3 \times 10^{-6}$  cm (lower scale of abscissas).

Curve B. Age 20 days, thickness  $10 \times 10^{-6}$  cm (lower scale).

Curve C. Age 30 days, thickness  $6 \times 10^{-6}$  cm (upper scale).

as the maximum decrease noted. Upon shutting off the light, there was no instantaneous change but a gradual and very slow decrease, indicating that the original resistance would be reached only after a very long time if at all. A graphical representation of these results is given in Fig. 5. It is interesting to compare these curves with those of Fig. 4.

The temperature appeared to have little effect upon the magnitude of this change.

Further investigation of this phenomenon is being carried on at this time in the hope of obtaining enough additional data to determine to what this effect is due. Perkins has called my attention to the fact that radiation has an effect upon the aging of bismuth films. He found that

screening greatly reduced the rate of increase of resistance. This was confirmed, a slight decrease in resistance being noted in one or two cases. These two phenomena may quite possibly be related. We may perhaps postulate a structural change such as that used to explain positive and negative light sensitive selenium; or we may find that this effect is in some way related to the magnetic properties of bismuth.

I wish to express my thanks to Professor A. T. Waterman, who suggested the problem, for continued assistance and interest, and to Professor J. Zeleny for his kindness in placing facilities at my disposal.

SLOANE LABORATORY,  
YALE UNIVERSITY,  
April 20, 1925.\*

\*First draft of article received July 15, 1924—Ed.



## A THEORY OF ELECTRICAL CONDUCTION IN METALS

BY ALFRED WOLF

## ABSTRACT

The electrons are assumed to have kinetic energy corresponding to the thermionic work function  $W$  and to move on orbits which form a space lattice with a constant  $\delta$  of the same order as that of the positive ions  $\delta_1$ . At each critical point of an orbit, each of the six directions are taken as equally probable. Treating the problem as a kind of Brownian motion and applying the virial theorem, the specific conductivity  $\sigma$  is found approximately equal to  $0.6 \times Ne^2(\delta^2/h)eW/\bar{E}$ , when  $\bar{E}$  is the mean heat content of one degree of freedom of the metal. The observed and calculated values of  $\sigma$  (taking  $\delta = \delta_1$ ) are in fair agreement for Ag, Au and Cu. For Na,  $\sigma(\text{obs.})$  is twice  $\sigma(\text{calc.})$ . Better agreement would be obtained if  $\delta$  were taken as  $1.5\delta_1$ , but uncertainty as to the values of  $W$  and as to the error introduced by applying the virial theorem to discontinuous processes makes this of little significance.

THE theory of conduction in metals, here presented, is based on the properties of space lattices and the theory of Brownian motion.

Recently J. Frenkel<sup>1</sup> and Hojendahl<sup>2</sup> developed views somewhat similar to those to be given. There are differences in essential points between Frenkel's theory and that presented here, but some developments have been modeled on Frenkel's views.

We shall regard a metal as a space lattice of positive ions in fixed positions (except for heat motion) and electrons moving on definite orbits between these ions, their motions being subject to quantum conditions. The paths of electrons we shall assume to form a space lattice in the metal. On this lattice electrons move in a disorderly fashion, at least as far as direction of motion is concerned. The space lattice constant  $\delta$  will be very closely related to the lattice constant of the metal  $\delta_1$ , e.g.  $\delta = \delta_1$  or  $\delta = 1.5\delta_1$ . The quantum conditions for the electrons should be applied between critical points of the lattice.

According to a well known theorem of mechanics, the mean kinetic energy of the electrons at absolute zero will be equal to the energy necessary to remove an electron from the metal, which in turn is equal to  $eW$ , where  $W$  is the thermionic work function and  $e$  is the electronic charge. For a discussion of this assumption and numerical calculations, reference

<sup>1</sup> J. Frenkel, *Zeits. f. Phys.* 29 (1924).

<sup>2</sup> Hojendahl, *Phil. Mag.* 48 (1924).

may be made to an article of J. J. Weigle.<sup>3</sup> At temperatures higher than the absolute zero we must have

$$\frac{1}{2}m\bar{v}^2 = eW + a\bar{E} \quad (1)$$

where  $\bar{v}^2$  is the mean square velocity of electrons,  $m$  the mass of an electron, and  $\bar{E}$  the mean heat content of one degree of freedom of the metal. The constant  $a$  will be of the order of unity, e.g.  $1/4$  or  $1/8$ . Equation (1) should not be interpreted as giving an increase of the heat content of the metal over the value given by Debye's theory, but rather as an expression of the fact that there is additional potential energy between electrons and ions due to the heat content of the body. In the theory of electrical conduction the quantity  $a\bar{E}$  can be neglected as compared with  $eW$ .

Let  $\tau$  be the time between instants of passing successive critical points by an electron. According to quantum conditions, we have  $h/\tau = 2eW$  or  $\tau = h/2eW$ .

As soon as an electron reaches one of these critical points all the directions in which it can move become equally probable and assuming the number of directions to be six, the probability that it will move a distance  $2\delta$  in a single direction is  $1/6$ . Similarly the probability of moving a distance  $k\delta$  in a single direction will be  $(1/6)^{k-1}$ . The mean square distance that an electron will move in one direction is therefore,

$$\lambda^2 = \delta^2 \frac{1 + 4(1/6) + 9(1/6)^2 + \dots}{1 + 1/6 + (1/6)^2 + \dots}$$

A different space lattice would change this expression only very slightly.

By employing a reasoning familiar from the theory of Brownian motion, we find that after crossing a critical point  $n$  times, the mean value of the square of the distance of an electron from its original position will be:

$$\overline{r_n^2} = n\lambda^2 = 1.8\delta^2 n \quad (3)$$

A type of reasoning similar to the above, but one which seems to the writer more rigorous, leads to a factor 1.4 in place of 1.8 in Eq. (3). In view, however, of the approximate nature of the assumptions involved, this alteration was neglected in the following. In the time  $t$  the electron crosses  $n = t/\tau$  critical points and consequently  $\overline{r_n^2} = 1.8\delta^2 t/\tau$  or, taking the component in one direction

$$\overline{x^2} = \frac{1}{3}\overline{r_n^2} = 0.6\delta^2 t/\tau \quad (4)$$

<sup>3</sup> J. J. Weigle, Phys. Rev. 25, 187 (Feb. 1925).

According to an equation given by Einstein<sup>4</sup> we also have

$$\overline{x^2} = 2Dt \quad (5)$$

where  $D$  is the coefficient of diffusion of electrons. No gradient of concentration of electricity can occur in a metal and the coefficient of diffusion assumes a meaning only if we distinguish between some class of electrons and the rest.

The action of an electric field on electrons will consist in imparting a certain momentum in the direction of the field at a uniform rate. If we consider the interaction of the electrons among each other it appears obvious that this momentum will be conserved. As however, from statistical and thermodynamic considerations, this increase of energy of electrons cannot be permanent, it must be transferred to the positive ions, thereby resulting in an evolution of heat. In an electric field therefore, the electrons will at first acquire a mean acceleration, but very soon the interaction with positive ions will cause them to give up as much momentum as they gain and their mean velocity in the direction of the field will then become constant in time.

An interaction of this kind will be represented by a viscosity coefficient  $\mu$ . In an electric field  $F$  the mean velocity will be  $(e/\mu)F$  and the conductivity becomes  $\sigma = Ne e/\mu = Ne^2/\mu$  where  $N$  is the number of valence electrons per unit volume of the metal.

Our object now will be to calculate  $\mu$ . The rate at which momentum is lost by electrons being  $\mu\dot{x}$ , we have

$$-\mu \sum \dot{x} = \sum M \ddot{X} \quad (6)$$

where  $M$  and  $X$  refer to positive ions and the summation is extended to all positive ions and electrons.

As the transfer of momentum takes place in a disorderly fashion with regard to coordinates, we have also, by the virial theorem,

$$-\mu \sum x \dot{x} = \sum M X \ddot{X} \quad (7)$$

or

$$-\frac{\mu}{2} \frac{d}{dt} (\overline{x^2}) = \frac{M}{2} \frac{d^2}{dt^2} (\overline{X^2}) - M \overline{X \ddot{X}}. \quad (8)$$

Considering that no diffusion of positive ions takes place and with regard to Eqs. (4) and (5) we find

$$(0.3\delta^2/\tau)\mu = \mu D = M \overline{X \ddot{X}} = \overline{E}. \quad (9)$$

<sup>4</sup> Einstein, Ann. der Phys. (1905).

The mean heat content of one degree of freedom of the metal can according to Debye be written as

$$\bar{E} = RT \frac{3}{(\theta/T)^3} \int_0^{\theta/T} \frac{x^3 dx}{e^x - 1}. \quad (10)$$

The equations (6) and (7) represent an application of the virial theorem to a discontinuous process and Eq. (9) can therefore be only approximately correct.

From (9) it follows that

$$\mu = 3.3 \tau \bar{E} / \delta^2 \quad (11)$$

and if we consider (2) the expression for conductivity  $\sigma$  becomes

$$\sigma = \frac{1}{3.3} N e^2 \frac{\delta^2}{\tau \bar{E}} = 0.6 N e^2 \frac{\delta^2}{h} \frac{eW}{\bar{E}}. \quad (12)$$

We shall now give a brief discussion of the limitations of the theory and compare the numerical values obtained from Eq. (12) with those actually observed.

In the first place as regards the variation of electrical conductivity with temperature it was shown above why (12) cannot be exact. Polarization of the ions and the quantity  $\alpha \bar{E}$  in Eq. (1) will, probably, be only of secondary importance. Qualitatively, however, the curve showing the heat content of solids is similar to that representing the resistivity of a metal and indeed formulas like  $1/\sigma \propto TC_v$  or  $1/\sigma \propto \hbar \nu / (e^{\hbar \nu / kT} - 1)$  have been proposed by various authors.<sup>5</sup> Quantitatively, the agreement is not very good; even for temperatures as high as 0°C the theory gives a temperature coefficient of resistivity 20 percent higher than observed (Ag, Cu, Au).

As regards the actual value of conductivity there are difficulties in the numerical interpretation of the quantity  $\delta$  in Eq. (12). For lack of any better value this was taken to be equal to the space lattice constant of the metal considered.

Below is given a table of observed and computed values for some univalent metals. The low calculated value of  $\sigma$  for Na will be explained below.  $W$  for Cu, Ag, Au was taken as 4 volts.

Metal:	Na	Cu	Ag	Au
$\sigma \times 10^{-4}$ (obs.):	22	64	67	45
(calc.):	10.6	61	50	47
$(1/\sigma)(d\sigma/dT)$ (obs.):	.0050	.0043	.0040	.0039
(calc.):	.0046	.0054	.0049	.0046

<sup>5</sup> Wien, Berl. Ber. 1913 (Part 1);

Grüneisen, Verh. Deutsch. Phys. Ges. 15 (1913) and 20 (1918);

Wereide, Ann. der Phys. 55, 589 (1918).

In view of the fact that the variation of resistivity with temperature is given only approximately, no exact agreement can be expected between the observed and calculated values of conductivity. If we consider that according to recent measurements the value of conductivity of a crystal of Cu is about 15 percent higher than that given above, we find that the order in which the metals Cu, Ag, Au are placed by the theory agrees with experiment.

There is one more point where the theory can be tested experimentally. According to Eq. (1) we have

$$\tau = \delta / \bar{v} = h / 2eW \quad \text{or} \quad \bar{v} = (2eW/h)\delta$$

and on the other hand

$$\sqrt{\bar{v}^2} = \sqrt{2eW/m}.$$

Metal:	Na	K	Cu	Ag	Au	
$\sqrt{\bar{v}^2}$ :	.8	.7	1.2	1.2	1.2	( $\times 10^8$ )
$\bar{v}$ :	.38	.39	.7	.8	.8	( $\times 10^8$ )

As a matter of fact we should have  $\bar{v} < \sqrt{\bar{v}^2}$  but the difference between the calculated values seems rather too large to be explained by that alone. In particular in the case of Na it seems to indicate that  $\delta$  is greater than the space lattice constant, a result which also explains the low value of  $\sigma$  obtained from Eq. (12).

It might seem at first sight that from the values of  $\sqrt{\bar{v}^2}$  and  $\bar{v}$  given above we might calculate the value of  $\delta$  and then substitute in the formula for conductivity. On account, however, of some uncertainty as to the numerical value of  $W$  only slight importance can be attached to that procedure.

In conclusion, it should be pointed out that an exact theory of conduction can probably be given only when the properties of the positive ions of the metal are taken into consideration. A considerable improvement could, however, be obtained by taking into account the discontinuous variation of momentum of electrons instead of using the virial theorem as has been done in this paper.

RESEARCH SECTION,  
RANDAL MORGAN LABORATORY,  
UNIVERSITY OF PENNSYLVANIA.  
March 25, 1925.

EFFECT OF TENSION UPON MAGNETIZATION AND  
MAGNETIC HYSTERESIS IN PERMALLOY

BY O. E. BUCKLEY AND L. W. MCKEEHAN

## ABSTRACT

**Magnetic properties of permalloy.**—*Effect of tension on magnetization and hysteresis.* Wires of 5 nickel-iron alloys containing 45, 65, 78.5, 81 and 84 percent Ni, 60 cm long and 0.1 cm in diameter, were studied by a ballistic method, for tensions up to 10,000 lb per in.<sup>2</sup> and fields up to saturation (10 to 20 gauss). Permalloy with 81 percent Ni is nearly indifferent to tension in its magnetic behavior; permalloy with less nickel is more easily magnetized and has less hysteresis when under tension, while 84 percent permalloy is more difficultly magnetized and has greater hysteresis when under tension. The saturation values are independent of the tension. In 78.5 percent permalloy, under a tension of 3560 lb per in.<sup>2</sup>, saturation is reached at only 2 gauss (and is practically complete at 0.2 gauss) and the hysteresis loss is only 80 ergs per cm<sup>3</sup> per cycle, so small that it may be regarded as due to slight inhomogeneity rather than to any essential features of the magnetization process. *Relation to crystal orientation.* X-ray examination proves that this abnormally low loss is not due to any peculiar orientation of the crystal axes as the crystals are found to be oriented at random. *Magnetostriction* behavior can be deduced from these results. Above 81 percent Ni, permalloy contracts like Ni while below 81 percent Ni, permalloy expands like Fe.

**Demagnetising factor for a wire** with a length 600 times the diameter, was determined experimentally and found to vary from a maximum of  $1.6 \times 10^{-4}$  to a low value, the changes being like these previously described by Benedicks for iron.

## INTRODUCTION

THE name permalloy has been given to a series of nickel-iron alloys so heat-treated as to possess initial permeability much in excess of that possessed by pure iron. Arnold and Elmen<sup>1</sup> announced the discovery of this material and gave a brief review of some of its properties. They noted the fact that the magnetic properties of permalloy are extremely sensitive to mechanical stresses and in particular that in certain samples, tension within the elastic limit reduced the permeability at certain low field strengths to one-tenth of its value in the unstressed sample. The work here reported is the result of a more detailed study of the effects of stress, undertaken in the hope that the behavior of permalloy in this regard would help to explain the fundamental process in magnetization.

## EXPERIMENTAL WORK

1. *Materials.* It was found by preliminary experiments that the effects of homogeneous tension and compression are opposite in sign,

<sup>1</sup> H. D. Arnold and G. W. Elmen, J. Frank. Inst. 195, 621-632 (1923).

and the former was chosen as easier to apply in the case of long samples. Wires of circular cross-section were used in obtaining the data here reported, although flat tapes like those used by Arnold and Elmen<sup>1</sup> gave similar results. A consideration of end effects, to be discussed below, led to the adoption of a standard diameter of about  $D=0.1$  cm and a standard length of about  $L=60$  cm, so that the dimension ratio  $L/D=600$ . The magnetizing solenoids extended over nearly the whole length of the sample, and the search coil, containing many thousand turns of fine wire, occupied about the middle quarter of its length. Under these conditions the results approximate to those that would be obtained with a ring sample unless the magnetic permeability much exceeds 10,000. Descriptions of the apparatus and methods employed in applying tension and in measuring changes in magnetization of the wire produced by changes in the applied field are contained in a recent paper by Cioffi,<sup>2</sup> to which the reader is referred for further details.

Previous work<sup>1</sup> had resulted in the accumulation of a series of alloys extending from nickel to iron by steps of 5 percent or less in nickel content, most of the alloys lying in the permalloy range, and containing, besides nickel and iron, about 0.2 percent manganese, 0.4 percent cobalt, and 0.2 percent non-metallic impurities. In order to compare these alloys annealed at 1000°C in vacuum, with others of higher purity, some stocks of iron and nickel were chemically purified, and 10-gram samples made up from these in different proportions were thoroughly mixed in the form of fine powder, compressed into blocks, sintered in vacuum, swaged, and drawn into wires of the standard size. The straight wires were then annealed for about an hour at 960°C in vacuum and allowed to cool to room temperature in about an hour. The samples so prepared are estimated to contain less than 0.05 percent total impurities. They are coarsely crystalline and for this reason somewhat unsatisfactory from a mechanical standpoint, the tensile strength being quite variable. Later experiments showed, however, that this crystalline structure, and the mechanical weakness resulting from it in certain cases, have little effect upon the magnetic properties of permalloy, so that we feel justified in regarding results obtained with these samples as characteristic of the compositions tested. The alloys of this series contained from 90 to 35 percent of nickel.

2. *Magnetic results.* The magnetic measurements were of two classes. In the first class the specimen was demagnetized and subjected to a series of alternating magnetizations with the desired applied field before the

<sup>2</sup> P. P. Cioffi, J. Opt. Soc. Amer. R. S. I., 9, 53-60 (1924).



change in induction through the search coil due to a single reversal of the field was measured. A series of such measurements for different applied fields gives a good approximation to the normal magnetization curve of the material provided that proper care is taken to compensate stray fields throughout the process.<sup>3</sup> Table I gives a typical set of data and results, the method of reduction being fully described below. Figs. 1 to 3, inclusive, exhibit normal magnetization curves as obtained in these experiments for five characteristic alloys, four of the purer series (84, 81,

TABLE I

*Representative calculations for 84 percent Ni, 16 percent Fe, (Fig. 1).*

Tension = 0;  $A = 0.426 \text{ cm}^2$ ;  $I_\infty = 780$ ;  $H_a(\text{initial}) = 0$ ;  $4\pi A_1 = 0.1029 \text{ cm}^2$ .

$H_a$ final	Gal- vanometer deflection	$\Delta\Phi$	$\Delta I'$ ( $=I'$ )	$\frac{I'}{I_\infty}$	$10^4 N$	$\Delta H$ ( $=H$ )	$I$
0.00196	6.0	0.063	0.60	0.001	1.600	0.00186	0.60
0.01000	29.8	0.314	3.02	0.004	1.600	0.00952	3.02
0.0176	54.5	0.573	5.50	0.007	1.600	0.01652	5.51
0.0352	113.2	1.191	11.34	0.015	1.600	0.0334	11.35
0.0587	205.8	2.16	20.8	0.027	1.600	0.0554	20.8
0.0929	23.0*	3.84	37.0	0.047	1.600	0.0870	37.0
0.166	59.3	9.91	95.6	0.123	1.600	0.1507	95.7
0.352	173.8	29.0	281	0.360	1.600	0.307	281
0.587	96.3*	41.7	404	0.519	1.600	0.522	404
0.978	120.0	52.0	502	0.644	1.596	0.898	503
1.56	139.5	60.5	581	0.745	1.586	1.468	582
4.62	171.0	74.1	702	0.900	1.382	4.52	703
9.82	188.6	81.7	754	0.966	0.794	9.76	754

\* Change in sensitivity of galvanometer.

65 and 45 percent nickel), and one of commercial purity, (78.5 percent nickel), in various conditions as to tension. In order to cover the great range in  $H$  and  $I$ , it has been necessary to use three sets of scales in each figure.

In the second class of experiments cyclic conditions were established between arbitrary limits in applied field, and the hysteresis loop between these limits was then obtained. The method of doing this and the precautions necessary for obtaining symmetrical loops have been dealt with elsewhere by McKeehan and Cioffi.<sup>3</sup> Table II gives a typical set of data and results. Figs. 4 and 5 exhibit hysteresis loops as obtained in these experiments for the same five samples as were used for the experiments of the first class.

<sup>3</sup> L. W. McKeehan and P. P. Cioffi, J. Opt. Soc. Amer. R. S. I. 9, 479-485 (1924).

Attention is particularly directed to the opposite character of the effect of tension in high-nickel and in low-nickel permalloy, to the relative indifference of the 81 percent Ni permalloy to tension, particularly in low

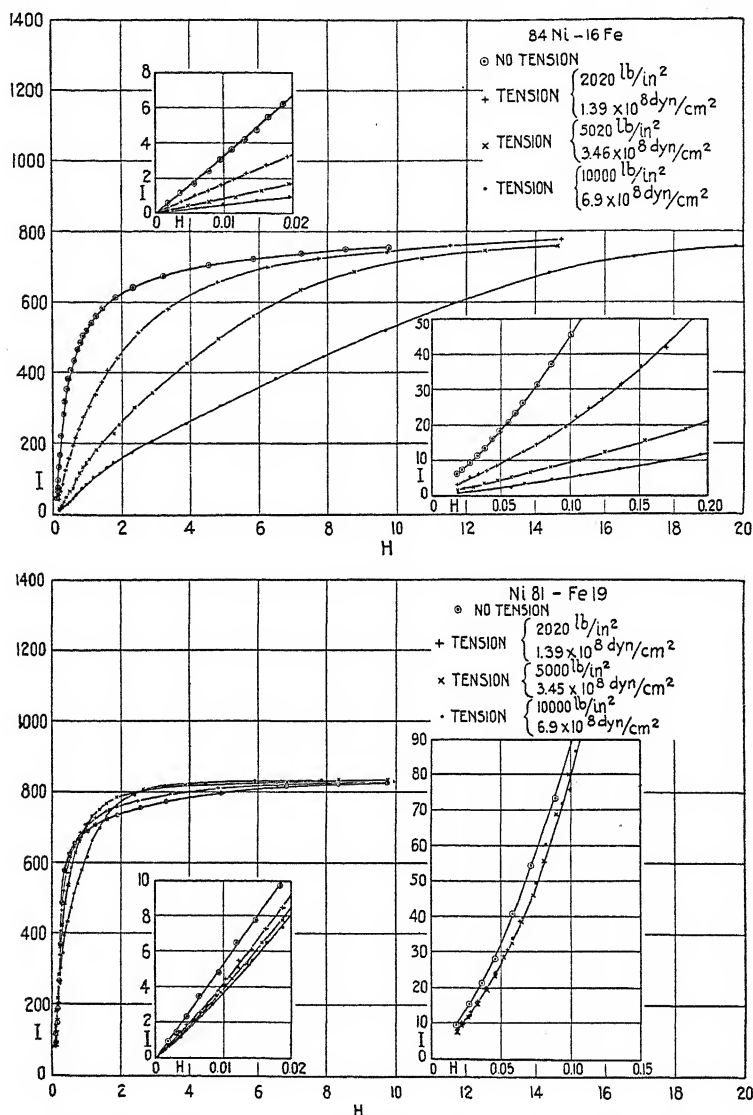


Fig. 1. Magnetization curves for 84 and 81 percent Ni permalloy; tension as indicated.

fields, and to the fact that the saturation values of magnetization are quite independent of tension. We will return below to a consideration of the significance of these results.

3. *Reduction of magnetic measurements.* The reduction of the data is theoretically very easy. The applied magnetic field  $H_a$  is proportional to the magnetizing current  $i$ . That is,

$$H_a = c_1 i. \quad (1)$$

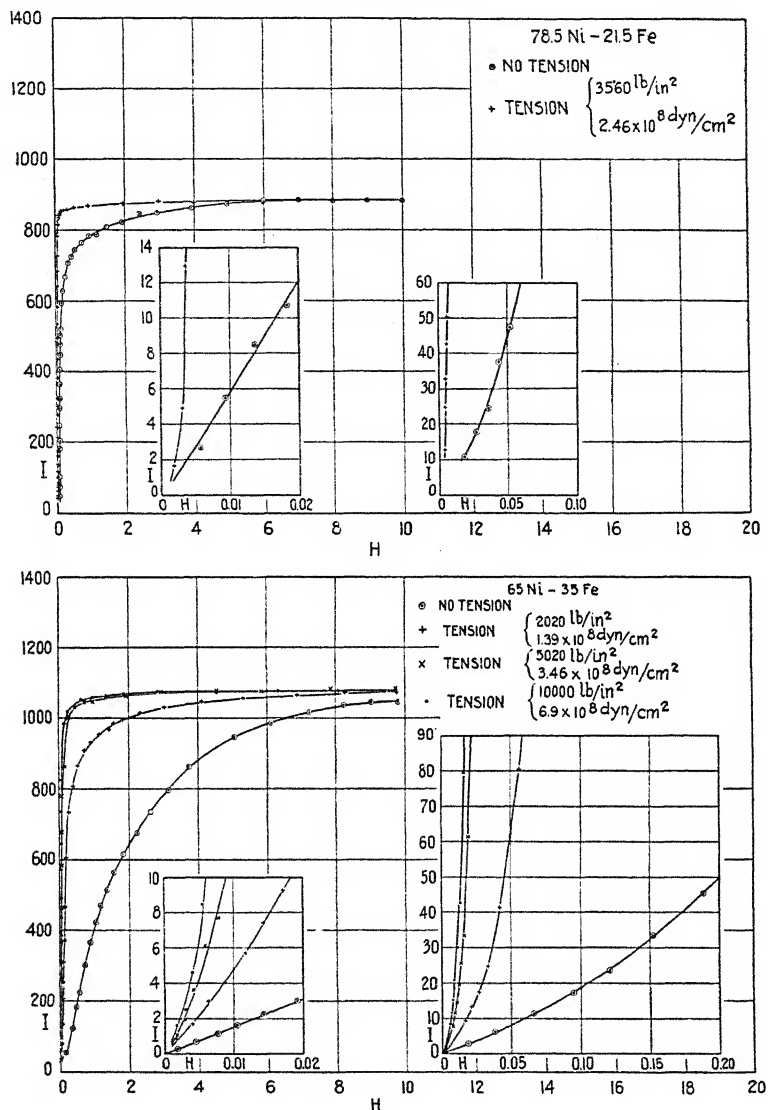


Fig. 2. Magnetization curves for 78.5 and 65 percent Ni permalloy; tension as indicated.

By the construction of the magnetizing coils, constant  $c_1 = 10$  gauss/amp.

The change of magnetic flux  $\Delta\Phi$  through a single search coil turn

(of mean area) is proportional to the galvanometer deflection  $\delta$ ; that is,

$$\Delta\Phi = c_2\delta. \quad (2)$$

Values of the constant  $c_2$  were determined by frequent calibration for the various series resistances used with each galvanometer to vary its sensitivity.

TABLE II

Representative calculations for 84 percent Ni, 16 percent Fe, (Fig. 6)  
Tension = 0;  $A = 0.426 \text{ cm}^2$ ;  $I_\infty = 780$ ;  $4\pi A_1 = 0.1029 \text{ cm}^2$ ;  $N = 1.600 \times 10^{-4}$ .

$H_a$ initial	$H_a$ final	Galv. defl.	$\Delta\phi$	$\Delta I'$	$I' (=I)$	$I'/I_\infty$	$H$
+1.000	+0.800	-114.0	- 2.28	-21.4	+462	0.592	+0.726
-1.000	-0.800	+115.2	+ 2.31	+21.7	-461	0.591	-0.726
+1.000	+0.300	- 96.0*	-11.66	-110.6	+372	0.477	+0.241
-1.000	-0.300	+96.0	+11.66	+110.6	-371	0.476	-0.240
+1.000	0.000	-190.6	-23.2	-222	+261	0.334	-0.042
-1.000	0.000	+190.0	+23.1	+221	-262	0.336	+0.042
+1.000	-0.150	-94.0*	-39.9	-384	+ 99	0.127	-0.166
-1.000	+0.150	+90.0	+38.2	+367	-116	0.149	+0.169
+1.000	-0.400	-190.0	-80.8	-780	-297	0.381	-0.352
-1.000	+0.400	+190.0	+80.8	+780	+297	0.381	+0.353
+1.000	-1.000	-235.8	-100.2	-966	-483	0.620	-0.923
-1.000	+1.000	+236.0	+100.2	+966	+483	0.620	+0.923

\* Change in sensitivity of galvanometer.

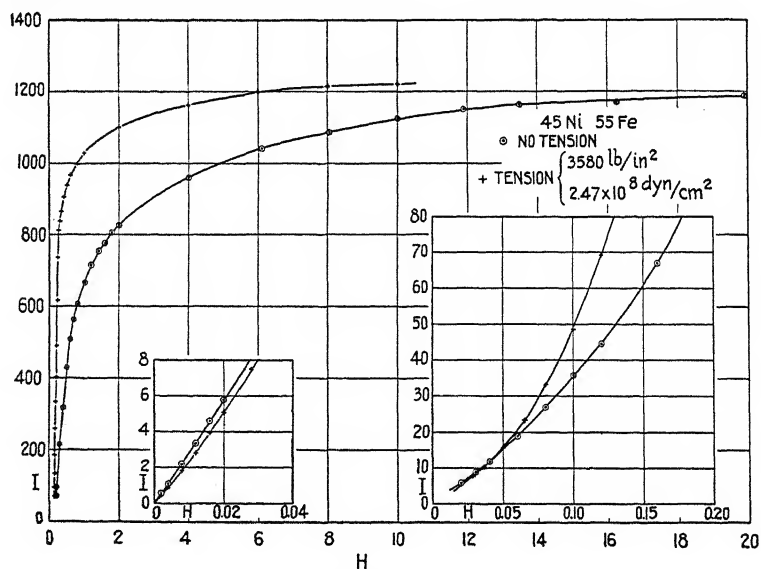


Fig. 3. Magnetization curves for 45 percent Ni permalloy; tension as indicated.

Let  $A$  = mean area of a turn of the search coil;  $A_1$  = area of cross-section of the sample;  $N$  = demagnetizing factor (due to limited length of sample);

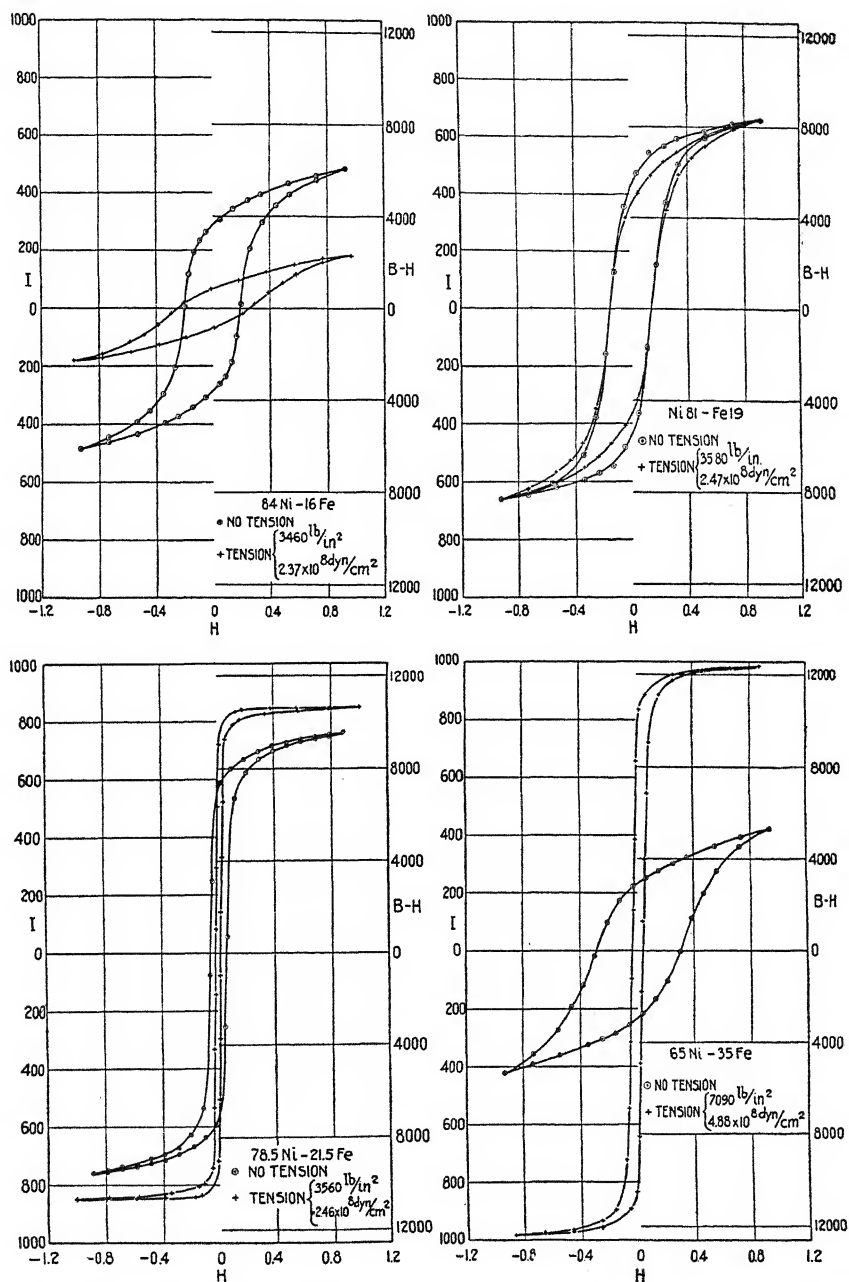


Fig. 4. Hysteresis loops for 84, 81, 78.5 and 65 percent Ni permalloy; tension as indicated.

$H$  = magnetic field within the sample, at the center of its length; and  $I$  = magnetization of the sample, at the center of its length. Then

$$\Delta I = (\Delta \Phi - A \Delta H_a) / (4\pi A_1 - NA); \quad (3)$$

$$\Delta H = \Delta H_a - N \Delta I. \quad (4)$$

If the simultaneous values of  $I$  and  $H$  are known for the initial state of the sample, say  $I_0$  and  $H_0$ , the general values in the  $n$ th succeeding state are obtainable from

$$I = I_0 + \sum_n \Delta I; \quad (5)$$

$$H = H_0 + \sum_n \Delta H. \quad (6)$$

The solution just given requires a knowledge of the value of  $N$ , which depends upon the shape of the sample and upon the distribution of magnetization within it. While  $N$  is calculable in a few cases there is no general agreement as to the value appropriate to the case of a very long

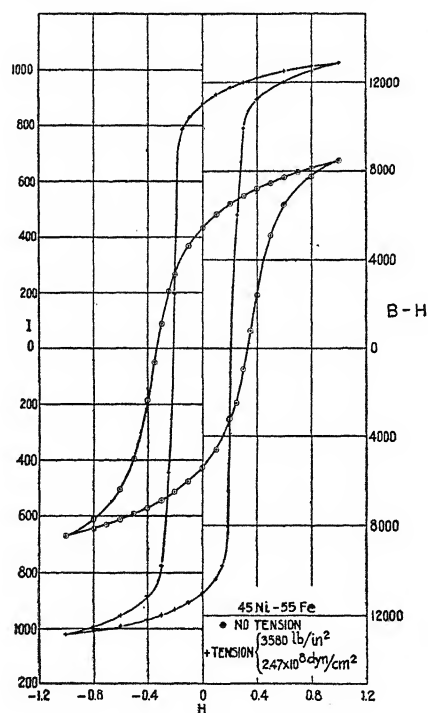


Fig. 5. Hysteresis loops for 45 percent Ni permalloy; tension as indicated.

cylinder.<sup>4</sup> In materials in which permeability rises as high as it does in some of the alloys here considered a difference in the choice of  $N$  between the permissible limits would greatly change our estimate of  $H$ . It is not even allowable to suppose that  $N$  is independent of  $I$  as is usually done.

<sup>4</sup> C. Benedicks, *Ann. der Phys.* (4), 6, 726-740 (1901); G. L. B. Schuddemagen, *Phys. Rev.* 31, 165-169 (1910); J. Wüschmidt, *Zeits. f. Phys.* 19, 388-397 (1923).

A separate experiment was accordingly performed in order to determine  $N$  as accurately as possible under the circumstances. A magnetic yoke was constructed, consisting of ten permalloy rods (78.5 percent Ni) each 1.1 cm in diameter, heat-treated so as to have high initial permeability and clamped at the ends in thick plates of similar permalloy, which were clamped in turn upon the ends of the wire under test. This complete cage of heavy permalloy formed both a return magnetic circuit and a magnetic shield.

TABLE III

*Representative calculations for 78.5 percent Ni, 21.5 percent Fe; (Fig. 6).  
Tension = 3560 lb/in<sup>2</sup> ( $2.46 \times 10^8$  dynes/cm<sup>2</sup>);  $H_a(\text{initial}) = 0$ .*

Without yoke				With yoke			
$H_a(\text{final})$	Galv. defl.	$\Delta\Phi$	$\Delta I' (= I')$	$H_a(\text{final})$	Galv. defl.	$\Delta\Phi$	$\Delta I' (= I')$
0.002	8	0.169	1.64	0.002	34.2	0.089	0.86
0.010	159	3.36	32.8	0.004	162	0.423	4.11
0.018	98*	8.09	78.9	0.006	35.0*	3.51	34.2
0.028	161	13.29	129.5	0.010	137	13.74	134.1
0.046	170*	21.8	213	0.014	76*	26.8	252
0.070	144*	33.4	326	0.018	110	38.6	377
0.110	236	54.8	534	0.024	138	48.4	473
0.150	171*	74.9	730	0.032	174	61.1	596
0.190	196.5	86.1	840	0.040	202	70.9	693
0.400	200.5	87.9	856	0.052	230	80.7	789
3.00	209	91.5	881	0.080	244	85.6	836
7.00	213	93.3	881	0.150	248.5	87.3	851
10.0	216.5	94.8	884	0.200	249.5	87.6	855

\* Change in sensitivity of galvanometer.

Table III gives a comparison between results obtained on the same sample, under the same tension, with and without the yoke. These are plotted in Fig. 6, upon which the correction  $NI = H_a - H$ , the difference of abscissas, has also been plotted as a function of  $I$ , the ordinate. Fig. 7 derived from the data used for Fig. 6, and other data of the same sort, gives  $N$  as a function of  $I/I_s$ , the relative saturation of the sample. In correcting the value of  $N$  for small variations from the standard diameter it has further been assumed that  $N/A_1$  is constant. In these experiments  $NA$  is always small compared to  $4\pi A_1$  so that it was found sufficient to use the approximate value,

$$\Delta I' = (\Delta\Phi - A\Delta H_a)/4\pi A_1 \quad (3')$$

in determining  $I'$  and from it the value of  $N$  (from Fig. 7 or a suitable table) to be used in computing  $\Delta I$  and  $\Delta H$ . This method of correction, of course, assumes the perfection of the magnetic yoke used in determining  $N$ . Any imperfection in the yoke leads to too low an estimation



of  $N$  and makes the investigated materials appear magnetically harder than they really are. It is thought, however, that the error from this source is unimportant. Figs. 3 and 5 are plotted from data taken with the aid of the yoke and therefore have not been corrected for end effects.

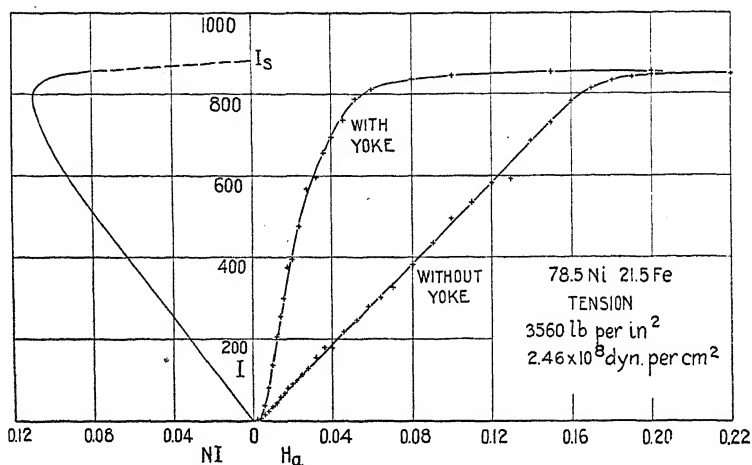


Fig. 6. Magnetization curves for 78.5 percent Ni permalloy, with and without yoke.

In order to show more clearly the enormous permeabilities here attained we have, in Fig. 8, compared the  $\mu$  vs  $B$  curves corresponding to Fig. 2

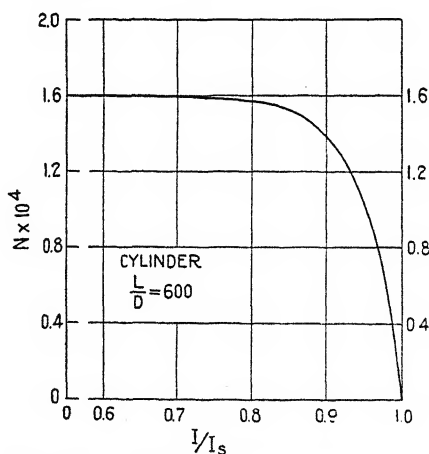


Fig. 7. Demagnetizing factor  $N$  for a cylinder with dimension ratio  $L/D=600$ .

(78.5 percent Ni) with representative curves for commercial grades of soft iron and silicon steel of good magnetic quality.

4. *X-ray examination.* Some theories of ferromagnetism have been based upon the assumption that the directions of easy magnetization in

any crystal are simply related to the crystal axes,<sup>5</sup> and it has recently been shown that the small crystals in wires and rolled sheet have certain preferred orientations.<sup>6</sup> It accordingly seemed possible at least that some of the results here obtained might be due to coincidence in direction of a particular crystalline direction with the axis of the wire. In order to test this hypothesis, samples were examined in an x-ray diffraction apparatus<sup>7</sup> by a method<sup>8</sup> which indicates whether preferred orientations exist or not. A preliminary search for such preferred orientations in the samples here studied showed an approximately random distribution of the crystal axes.

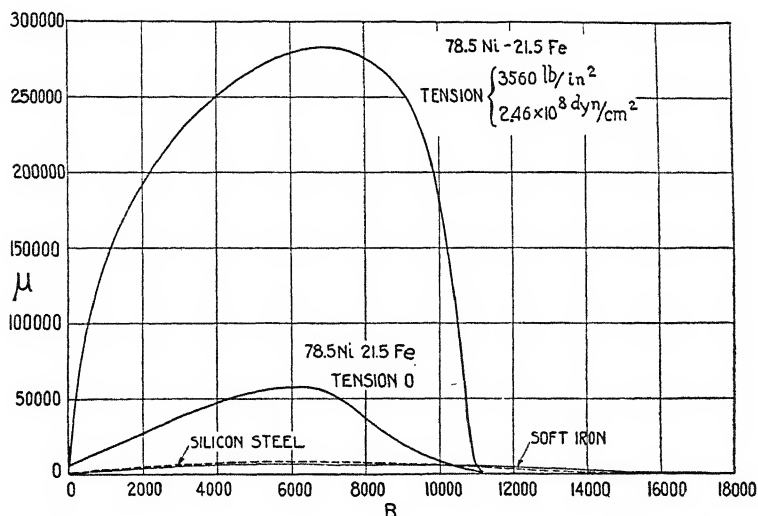


Fig. 8. Permeability curves for 78.5 percent Ni permalloy compared with curves for commercial magnetic iron and silicon steel.

#### DISCUSSION OF RESULTS

It has long been known that magnetostrictions in iron and nickel are of opposite sign, iron increasing in length in weak magnetic fields and nickel diminishing in length in all fields. It has also been reported by Honda and Kido<sup>9</sup> that nickel-iron alloys show a change in the sign of their magnetostriction at a composition not far from 80 percent nickel. The samples used by these investigators were small castings and the fields employed were relatively intense so that it was not at first sight

<sup>5</sup> J. Kunz, Bull. Nat. Res. Council, **3**, [3], 165-213 (1922).

<sup>6</sup> M. Ettisch, M. Polanyi and K. Weissenberg, Zeits. f. phys. Chem. **99**, 332-338 (1921).

<sup>7</sup> W. P. Davey, J. Opt. Soc. Amer. R. S. I. **5**, 479-493 (1921).

<sup>8</sup> R. M. Bozorth, Phys. Rev. (2) **23**, 764 (1924).

<sup>9</sup> K. Honda and K. Kido, Tohoku Univ. Sci. Rep. **9**, 221-232 (1920).

obvious that magnetostriction in permalloy in weak fields should also change sign in this region. The results presented above, however, fully support the statement that high-nickel permalloy contracts, like nickel, and low nickel permalloy expands, like iron, in the direction of the applied field. The measurement of the effect of tension upon magnetization is, in fact, more convenient as an indicator of the sign of magnetostriction than is direct measurement. As far as our experiments go, the change in sign of magnetostriction occurs somewhere between 80 percent and 83 percent of nickel. There is probably no point at which magnetostriction is entirely absent unless we limit consideration to some particular applied field, since, as Fig. 2 indicates, the sign of the effect of tension upon magnetization in 81 percent nickel permalloy may change several times in the process of saturating the material.

TABLE IV  
*Hysteresis losses*

Material	Tension (lb/in <sup>2</sup> )	Maximum $\beta$	Losses (ergs/cm <sup>3</sup> /cycle)
84% Ni; 16% Fe	None	6100	300
	3460	2260*	120
81% Ni; 19% Fe	None	8320	350
	3580	8320	310
78.5% Ni; 21.5% Fe	None	9560	180
	3560	11000	80
65% Ni; 35% Fe	None	5300*	370
	7090	12400	160
45% Ni; 55% Fe	None	8500*	680
	3580	12900	830
Silicon steel		14000	4500
Soft iron		15000	6500
Tungsten magnet steel		16000	275,000
K. S. magnet steel		16000	900,000

\* Far from saturation.

The low values of hysteresis loss here attained indicate to us that hysteresis is a secondary phenomenon not essential in an ideal ferromagnetic material. Although the narrowest hysteresis loops here plotted still show an appreciable area it should be noted that the scale chosen is such that the width of the loops is greatly exaggerated. How small the hysteresis has really become can best be shown by comparing the approximate areas of hysteresis loops for various magnetic materials, including those here tested, some of which run nearly to saturation. Such a comparison is given in Table IV. Since it is unreasonable to suppose that

any of the samples tested were perfectly homogeneous, it may well be that in small regions hysteresis completely disappeared in certain of the experiments.

The generalizations which have been based upon the work of Weiss and others, who have studied the magnetization of large crystals of magnetite, pyrrhotite, and silicon iron<sup>5</sup> seem to us altogether too sweeping. In particular, the fact that practically complete magnetic saturation of randomly oriented crystals has here been obtained in low fields disproves the hypothesis that particular directions within any ferromagnetic crystal are the only ones in which magnetization is easy. This and other theoretical bearings of this work are discussed by McKeehan in a succeeding paper.<sup>10</sup>

The progress of this study has depended upon the cooperation of so many individuals that it will be impossible to make an acknowledgement of our indebtedness to all of them. It may be stated, however, that the preparation of the pure samples was conducted by Mr. H. T. Reeve, the x-ray examinations by Dr. R. M. Bozorth, and that the magnetic data were taken by Mr. P. P. Cioffi to whom also are due many of the experimental refinements which permitted accurate and rapid measurements under magnetically unfavorable conditions.

BELL TELEPHONE LABORATORIES, INCORPORATED,  
NEW YORK, N. Y.  
April 3, 1925.

<sup>10</sup> L. W. McKeehan, following paper in this issue.

## A CONTRIBUTION TO THE THEORY OF FERROMAGNETISM

By L. W. MCKEEHAN

## ABSTRACT

Relation of permeability and hysteresis to atomic magnetostriction.—In permalloy, as shown in the preceding paper, magnetostriction changes sign at about 81 percent Ni, hysteresis losses can be made vanishingly small near this composition, and these effects are not due to the special alignment of crystals. It is suggested that in every ferromagnetic material the process of magnetization involves (1) intra-atomic changes, presumably changes in the orientation of electron orbits, governed by quantum dynamics and independent of environment; and (2) inter-atomic changes (stresses and strains). The inter-dependence of the inter-atomic changes and the intra-atomic changes is conveniently described as atomic magnetostriction. On this view, hysteresis loss and magnetic hardness are due to the energy required to produce, in succession, the local deformations associated with changes in the magnetization of single atoms or small groups of atoms. High initial permeability and low hysteresis loss in permalloy are explained as resulting from locally compensatory atomic magnetostrictions of the nickel and iron atoms in small groups. The fundamental differences in the magnetic behavior of Fe, Ni and Co are attributed to differences in their atomic magnetostrictions. Other differences are attributed to differences in the mechanical properties which alter the energy expended when atomic magnetostriction takes place.

THE fact that certain nickel-iron alloys are much more easily magnetized than either nickel or iron is not explained by any existing theory of ferromagnetism. Ewing's suggestion, made many years ago, that soft annealed iron probably has less coercivity than any other magnetic substance,<sup>1</sup> still appeared plausible until the announcement of the discovery of permalloy.<sup>2</sup> The explanation of permalloy demands, therefore, some revision of our ideas regarding ferromagnetism in general.

From the very beginning, it has been evident that discontinuities of some kind had to be introduced into the explanation of ferromagnetism, so that it is here perhaps that the quantum theory should have had its most natural application. Delay in making such an application has occurred, it would seem, because hysteresis has been so conspicuous in ordinary magnetic materials that the reversible processes discussed by the quantum theory have been obviously unsuitable to explain all of the facts to be covered by an adequate theory.

<sup>1</sup> J. A. Ewing, *Magnetic Induction in Iron and Other Metals*, 3rd edition, 1900, p. 315.

<sup>2</sup> H. D. Arnold and G. W. Elmen, *J. Frank. Inst.* 195, 621-632 (1923).

In seeking the cause for the inadequacy of the older theories it is necessary to discover where each of them introduced unwarranted hypotheses. A recent review<sup>3</sup> makes comparison between the older theories particularly easy. It appears after a little study that none of them has taken sufficient notice of the fact that the medium, the behavior of which they attempt to describe, is really discontinuous. Some<sup>4</sup> of the theories are quite obviously faulty in this respect, introducing intrinsic fields of force to a greater or less extent, and thereby avoiding consideration of the physical basis of magnetic retentivity and hysteresis. Others<sup>5</sup> begin with the atoms but introduce what amounts to the assumption of a continuous medium when large groups of atoms are pictured as undergoing simultaneously equal changes in magnetization.

A theory free from the objection just raised has recently been proposed by Ewing<sup>6</sup> and is sufficiently physical in its basis to permit of experimental test. It demands considerable complexity within the ferromagnetic atom since it regards the principal ferromagnetic characteristics as all due to intra-atomic properties. It, too, suggests no reason for the peculiarities found in permalloy and, in fact, seems to deny the possibility of their occurrence, since in an alloy we would not expect to find the individual atoms more symmetrically surrounded by their neighbors than in a pure metal, and Ewing's new theory makes a highly symmetrical environment of every atom essential to magnetic softness.

Magnetostriction,<sup>7</sup> the change in dimensions accompanying magnetization, has proven even more difficult to explain than ferromagnetism itself. No quantitative agreement has been reached between predictions based on theories of magnetostriction and the observed effects of mechanical stress upon magnetization. It should be noted that these theories also disregard the atomic structure of matter.

Until a short time ago it was permissible to postulate within the ferromagnetic atom almost any sort of mechanism which seemed necessary to the theorist. Now, however, that information is available in regard to the magnetic behavior of silver vapor<sup>8</sup> and the paramagnetism of ions in solution<sup>9</sup> it appears that the atomic structures responsible for magnet-

<sup>3</sup> E. M. Terry and J. Kunz, *Bull. Nat. Res. Coun.* **3**, [3], 113-213 (1922).

<sup>4</sup> Theories of Weiss, Frivold, Gans, loc. cit.<sup>3</sup>

<sup>5</sup> Theories of Ewing, Honda, Honda and Okubo, loc. cit.<sup>3</sup>; cf. K. Honda, *Dictionary of Applied Physics*, **3**, 515-526 (1922).

<sup>6</sup> J. A. Ewing, *Proc. Roy. Soc. A100*, 449-460 (1922).

<sup>7</sup> S. R. Williams and S. L. Quimby, *Bull. Nat. Res. Coun.*, **3**, [3], 214-234 (1922).

<sup>8</sup> W. Gerlach and O. Stern, *Zeits. f. Phys.* **8**, 110-111 (1921); **9**, 349-352, 352-353 (1922).

<sup>9</sup> B. Cabrera, *Journ. de Phys.* (6), **3**, 443-460 (1922).

ism cannot be very different from those already proposed to explain the emission and absorption of radiation.<sup>10</sup> The fact that ferromagnetism occurs in a very limited group of elements in the atomic series appears<sup>11</sup> to support the conclusions as to atomic structure derived by applications of the quantum theory to optical and x-ray emission and absorption spectra. If the arguments in favor of these structures are sound there is no place left within the ferromagnetic atoms for special mechanisms to account for magnetic hysteresis or other causes of energy dissipation on a large scale.

It is the purpose of this paper to show how division of the problem of ferromagnetism into two parts, and the introduction of a suitable connecting link between these parts permits the construction of a simple theory adequate to explain the new experimental results and consistent with what we already know of atomic structures and atomic processes.

The most natural possible division is that between processes which occur wholly within single atoms and processes which involve more than one atom, i.e., between intra-atomic and inter-atomic processes.

The first assumption will be that intra-atomic changes are governed by quantum dynamics, and in particular that the component, parallel to the applied field, of the magnetic moment of any individual atom changes abruptly, if at all. Such changes in the magnetization of an atom will occur, one after another, as the applied field is gradually raised to values which can supply the necessary energy. It need not here be considered whether or not a very weak applied field will establish a single direction within the material, with respect to which the magnetic moment of every atom is spatially quantized. Neither is it important for the present purpose to decide whether or not the absolute value of the magnetic moment of an atom, or only the direction of its axis, undergoes abrupt changes. The essential thing implied by the first assumption is that the principal changes in magnetic moment parallel to the applied field are to be considered as abrupt and as spatially discrete.

The second assumption will be that an abrupt change in the magnetization of an atom, of the sort just postulated, is accompanied by a change in that atom which is independent of the environment in which it may be placed.<sup>12</sup> This change affects the forces which the atom exerts upon its

<sup>10</sup> W. Gerlach, *Phys. Zeits.* **24**, 275-277 (1923); P. S. Epstein, *Science* (2), **57**, 532-533 (1923); A. Sommerfeld, *Phys. Zeits.* **24**, 360-364 (1923); *Zeits. f. Phys.* **19**, 221-229 (1923).

<sup>11</sup> R. Ladenburg, *Zeits. f. Elektrochem.* **26**, 262-274 (1920); N. Bohr, *Zeits. f. Phys.* **9**, 1-67 (1922); L. W. McKeehan, *J. Frank. Inst.* **197**, 583-601, 757-786 (1924).

<sup>12</sup> The logical necessity for assuming the change to be independent of the characteristics of neighboring atoms was pointed out by Professor P. Ehrenfest in a private discussion.



neighbors so that the body of which it is a part tends to change in dimensions. The nature of the changes in forces which take place may be inferred from the change in the over-all dimensions of measurable bodies consisting wholly of atoms of the kind considered. The atomic changes which must occur to explain gross magnetostriction will conveniently be designated as atomic magnetostriction.

The third and final assumption is that magnetic hardness and hysteresis in measurable amount are due primarily to inter-atomic stresses set up by atomic magnetostriction, and therefore are dependent not only upon the type of atom which is magnetized but also upon the mechanical properties of the particular piece of metal of which it forms a part. In hard magnetic materials the changes involved in atomic magnetostriction meet great resistance and require the supply to the atoms, through the application of intense magnetic fields, of large amounts of energy. In soft magnetic materials the same changes meet little resistance and can therefore occur in weaker applied fields.

Hysteresis is to be regarded as due to the shocks upon the structure resulting from the sudden changes of force between atoms involved in atomic magnetostriction. A part of the energy so emitted by the atom will be dissipated at once, appearing as heat. Another part will be stored temporarily as potential energy of local strains. If these strains are relieved by further magnetization their energy will also degenerate into heat. If not, a part of this energy will be available for demagnetizing the material when the applied field is diminished, thus being responsible for the difference between the values of saturation intensity and remanence in closed magnetic circuits.

Externally applied agents, with the single exception of magnetic fields, must be supposed to act upon the magnetization of the individual atoms through their primary effect upon those inter-atomic forces which can also be set up or altered by atomic magnetostriction. Crystalline structure, affecting as it does the distribution and magnitude of such forces in different directions, should have, in pure materials at least, a considerable effect upon magnetization in different directions.

The cause of atomic magnetostriction is to be looked for in the changes of electronic arrangement which occur when the atom changes its magnetization. Speculations have been made upon this phase of the subject<sup>13</sup> but the details are unessential to the argument here presented.

The magnetization of a pure metal, consistently with these assumptions, may be pictured as follows. Slight inhomogeneity of conditions

<sup>13</sup> L. W. McKeehan, loc. cit.<sup>10</sup>

throughout the material will determine the spatial distribution of the atoms which change their magnetic states in a weak applied field. Further magnetization of the atoms originally affected, or of adjacent atoms of the same kind, will be hindered by the forces set up by atomic magnetostriction, i.e. the further increase of these forces against the elasticity of the material will require an increase in the applied field. The process at first proceeds, therefore, by the successive magnetization of widely distributed atoms. The distribution of these atoms, located at points where the unfavorable stresses are least, tends to become more uniform as the field is increased. Consideration of the unmagnetized atoms shows that at first the number of these which are similarly situated with respect to those already magnetized will increase, affording a supply of atoms capable of changing their magnetic states at about the same value of applied field in a later stage in the process. When this group is being magnetized the rate of increase in permeability reaches a maximum in what has recently been described as the leg<sup>14</sup> of the magnetization curve. It is in this stage of the process that the Barkhausen effect (noise of magnetization) is also a maximum.<sup>15</sup>

The remarkable ease with which permalloy may be magnetized is striking evidence for the correctness of the theory outlined in the preceding paragraphs. Nickel, as is well known, shortens when longitudinally magnetized, while iron, at least until it is almost completely saturated, lengthens under the same conditions. Their gross magnetostrictions being opposite in kind the second assumption demands that their atomic magnetostrictions also be opposite in kind, and that this difference persist in nickel-iron alloys. It is accordingly to be expected in these alloys that local stresses set up, for example, by the magnetization of a nickel atom will be partly relieved by magnetization of an adjacent iron atom, and vice versa. Magnetization in a properly proportioned alloy of this type should be able to spread continuously from any point where it begins and should require but little increase in the applied magnetic field to produce saturation. The proper proportion of nickel and iron should be about that at which gross magnetostriction vanishes.<sup>16</sup> Hysteresis should be much diminished by the simultaneous magnetization of small groups of nickel and iron atoms in such proportion that the changes in the forces exerted by the group upon its neighbors is a minimum. Such cooperative changes, requiring little energy, should be rela-

<sup>14</sup> V. Karapetoff, *Science* (2), 59, 440 (1924).

<sup>15</sup> E. P. T. Tyndall, *Phys. Rev.* (2), 24, 439-451 (1924).

<sup>16</sup> O. E. Buckley and L. W. McKeehan, preceding paper in this issue.

tively probable, as compared with changes in the magnetization of single atoms. The remanence should be relatively great because no considerable unrelieved strains would ever exist during the process of magnetization. Since inter-atomic forces would be modified but little during the entire process, the effect of crystalline structure should be, as it is,<sup>16</sup> unimportant in such a material.

It will be observed that the fundamental differences in magnetic behavior between the three ferromagnetic elements are here to be attributed to differences in their atomic magnetostrictions, and that the modifications in the magnetic characteristics of a single element by alloying, heat-treating, or mechanical working are to be attributed to differences in the readiness with which local strains may be set up and relieved. That condition of each magnetic material in which it is most difficult to produce the types of local strain associated with its atomic magnetostriction should be magnetically hardest. The close connection between magnetic and mechanical hardness is a strong argument in favor of the reality of atomic magnetostriction.

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## BOOK REVIEWS

**The Structure of Matter.** J. A. CRANSTON.—Most of the books on the structure of matter which have appeared during the last few years are either popular books intended for the general public or strictly technical works intended primarily for physicists. This latest volume attempts to bridge the gap between these two sorts of books. It is written, in the editor's phrase, "by a physical chemist for chemists" and is therefore non-mathematical. It should be useful not only to chemists but to beginners in physics, to secondary school science teachers, engineers and others prepared to follow a semi-technical discussion.

The principal topics taken up are the determination of the charge and mass of the electron, radioactivity, the scattering of alpha particles and the nuclear theory of the atom, x-rays and crystal structure, atomic models, and Langmuir's valency theory.

The book is clearly written, up-to-date, and, so far as the reviewer can judge, accurate. The only adverse criticism which it arouses has to do with the question of emphasis and the choice of topics treated. No mention is made of photo-electricity, fluorescence, and band spectra. Ionizing potentials are introduced in one brief paragraph only to make connection with J. J. Thomson's atomic model. Ten brief pages are given up to the whole Bohr theory, while over fifty are devoted to the Lewis cubical atom and the Langmuir valency theory! These omissions would occasion little comment were it not for the suggestion in the preface that the material in this volume will suffice to bring the old-fashioned chemist up to date and the intimation of both author and editor that this is a review of the whole subject. Physicists will not be misled, but it seems unfortunate that chemists should be encouraged in this day and age to believe that they can get along very well in ignorance of the quantum theory and the experiments on which it is based.—196 pages, 70 figures. D. Van Nostrand Co., 1924. \$4.50. E. C. KEMBLE.

**Die Kultur der Gegenwart; Physik.** Edited by E. LECHER.—The first edition of the volume on Physics in the series "Die Kultur der Gegenwart" was edited by Professor Warburg and published in 1914. Its purpose was to provide a comprehensive account of the whole of Physics, to give a historical development of the fundamental ideas of each branch of the science leading to our present concepts, and to show the relations of the different branches to each other. This second edition, edited by Professor Lecher, has been thoroughly revised so as to give an account of the developments during the last ten years.

The authoritative character of the work may be judged from the names of the contributors to the volume. Thus Wiechert writes on Mechanics, Auerbach on Acoustics; the section on the Theory of Heat has contributions from Warburg, Holborn, Hemming, Jaeger, Hettner, W. Wien, Przibram, and Einstein; Electricity and Magnetism is treated by Richarz, Lecher, Lorentz, Gans, Gumlich, Braun, M. Wien, Starke, Kaufmann, Gehrke and Reichenheim, Elster and Geitel, and St. Meyer and Schweidler; Light and Spectroscopy by Wiener, Lummer, v. Rohr, Exner, Gehrke, Zeeman and Kramers; while a concluding section on general laws and points of view is written by Warburg, Hasenöhr, Mache, Planck, Einstein and Voigt.

The treatment throughout is almost entirely descriptive, in accordance with the object of the volume, with the least possible use of mathematical symbolism. It is not, of course, a book of reference for details. At the same time it is not a book for beginners. It would be an excellent book for study by first-year graduate students in our Universities, covering, as it does, what candidates for the doctor's degree should be expected to know of general Physics in its historical and philosophical aspects. There is a real need of a similar book in English, and a translation of this volume would undoubtedly fill a long-felt want.—Pp. viii+849. Teubner, Leipzig and Berlin. 1925. 36 Marks, bound. E. P. ADAMS.

PROCEEDINGS  
OF THE  
AMERICAN PHYSICAL SOCIETY

MINUTES of the PORTLAND MEETING, June 19, 1925

The 134th regular meeting of the American Physical Society was held in Portland, Oregon, at the Laboratory of Physics, Reed College, on Friday, June 19, in affiliation with the Pacific Division of the American Association for the Advancement of Science. The meeting of that Association included a research conference, Wednesday, June 17, and other meetings and excursions extending through Saturday, June 20.

The session of the Physical Society consisted of twenty-four papers of which abstracts are given in the following pages. Numbers 15 and 16 were presented by title. An **Author Index** will be found at the end.

The attendance was about 100.

D. L. WEBSTER  
*Secretary, Pacific Coast Section.*

ABSTRACTS OF PAPERS

1. Quantum theory of the number of beta-rays associated with scattered x-rays. G. E. M. JAUNCEY and O. K. DEFoe, Washington University, Saint Louis.—A. H. Compton and A. W. Simon (Phys. Rev. 25, 306, 1925) have recently measured the ratio of the number of recoil electron tracks to that of the photo-electron tracks in a Wilson cloud apparatus. For short wave-length x-rays the experimental ratio was found equal to  $\sigma/\tau$  as predicted by the theory of Compton and Hubbard (Phys. Rev. 23, 439, 1924). For the long wave-lengths, however, the experimental ratio is distinctly smaller. In the present paper a correction factor is applied to  $\sigma/\tau$  by taking into account the motion and the binding energy of the scattering electron in its Bohr orbit, as done by Jauncey (Phys. Rev. 25, 314, 1925), and also the minimum energy which the recoil electron must have in order to produce a visible track. Assuming a minimum energy of 630 volts for a recoil electron to produce a visible track, the correction factor for a primary wave-length of 0.71A is 0.36, thus making the theoretical value of the ratio of recoil to photo-electron tracks 0.097 as against an experimental ratio of 0.10. For other wave-lengths the agreement is equally good.

2. X-rays scattered by molybdenum. P. A. Ross, Stanford University.—Using an ionization spectrometer and a standard water-cooled molybdenum Coolidge tube, the radiation scattered by the molybdenum cathode cup of the tube itself has been measured at 110° and 160° scattering angle. The shift of the modified line at 110° was  $.035 \pm .002A$ .

The theoretical value is .0345A. At  $160^\circ$  the measured shift was  $.047 \pm .002A$  and the computed value .0469A. The unmodified line was completely obscured by the intense fluorescent line coinciding with it and making any estimate of relative intensity impossible. Radiation scattered from the glass was measured by slightly displacing the tube so that the line of slits just missed the cathode cup. The glass scattering was small compared with that by the cathode. Using a standard tungsten Coolidge tube and the same method of procedure the scattering of tungsten K radiation from molybdenum was observed. At  $160^\circ$  scattering angle the tungsten K $\alpha$  line was shifted by  $.047 \pm .001A$ . The ratio of intensity of modified to unmodified line was .10 but this was probably too low due to fluorescence of the thin coating of tungsten deposited on the cup.

3. The ratio of intensity of the Compton lines. P. A. ROSS, Stanford University.—The spectrograms of scattered x-rays taken by the writer alone and in collaboration with D. L. Webster have been studied by means of a photographic densitometer. This has permitted the determination of the intensity ratio of modified to unmodified line (see last column of Table) for various scattering materials and also more precise measurement of the magnitude of shift due to the more accurate determination of the center of gravity of the lines.

Scattering substance	Incident radiation	Scattering angle	Shift ( $10^{-3}A$ )	Ratio of intensities
graphite	Mo K $\alpha$	$30^\circ$	$3. \pm 1$	0.2
		$60^\circ$	$12.0 \pm 0.1$	0.95
		$90^\circ$	$23.6 \pm 0.3$	1.7
aluminum	Mo K $\alpha$	$90^\circ$	$24.4 \pm 0.1$	0.7
aluminum	Mo K $\beta$	$90^\circ$	$24.2 \pm 0.1$	1.0
sulfur	Mo K $\alpha$	$90^\circ$	$24.0 \pm 0.5$	0.29
copper	Mo K $\alpha$	$90^\circ$	$24.4 \pm 0.2$	0.32
silver	Mo K $\alpha$	$90^\circ$	$23.8 \pm 0.2$	0.21
lead	Mo K $\alpha$	$90^\circ$	$24.0 \pm 0.2$	0.024

4. Spectrograms of tungsten K series rays scattered by graphite. M. C. MAGARIAN, Stanford University.—Spectrograms of tungsten K rays scattered by graphite were obtained showing the shifted and unshifted K $\alpha$  lines. The shifted line was much more intense than the unshifted line. The shift in wave-length showed fair agreement, within the probable errors, with the theoretical value given by Compton's relation. For a measured scattering angle of  $92^\circ \pm 2^\circ$  this relation gives a change in wave-length of  $0.025 \pm .001A$ , whereas the measured change in wave-length was  $0.027 \pm .003A$ . The chief source of error came from the measurement of the separation between the shifted and unshifted lines on account of the faintness and lack of sharpness of the lines. The x-rays were obtained from a Coolidge tube with a mechanically rectified current of 5 milli-amperes at 120,000 volts. The spectrometer consisted of a Seeman slit with a calcite crystal and ten photographic plates all of which were mounted on a base.

5. Series spectra of B<sub>II</sub> and C<sub>III</sub>. I. S. BOWEN and R. A. MILLIKAN, California Institute of Technology.—By the methods previously reported in our development of hot-spark spectrometry, the following term values of B<sub>II</sub> have been determined:  $2S=194325.9$ ;  $3S=66665.1$ ;  $2P=120929.4$ ;  $3D=48410.3$ ;  $3s=72930.8$ ;  $4s=36655.5$ ;  $2p_1=165343.9$ ;  $2p_{2,3}=165362.7$ ;  $3p_1=59006.5$ ;  $3p_{2,3}=59010.0$ ;  $3d=52054.2$ ;  $4d=28640.4$ ;  $4f=27800.0$ ;  $5f=17795.7$ . The following term values of C<sub>III</sub> have also been found:  $2S=375463.1$ ;  $2P=273111.0$ ;  $3s=146197.2$ ;  $2p=331939.2$ ;  $3p_1=124685.8$ ;  $3p_2=124698.6$ ;  $3p_3=124704.1$ ;  $3d=114387.2$ ;  $4f=62600$ .

6. Series and multiplets in sulfur and chlorine. J. J. HOPFIELD, University of California.—Some time ago the author published some new sulfur series, (Nature 112,



437, 1923). These have been rechecked. The frequencies are given by the following equations:

$$\nu = 83554 - R/(n + 1.05086 - 0.13386/n + 0.05425/n^2); n = 1, 2, \dots$$

$$\nu = 83554 - R/(n + 0.53341 + 1.06794/n - 0.82152/n^2); n = 2, 3, \dots$$

The series' head is indicated only for the highest members of the triplets. By the use of these series the unassigned lines of sulfur (Fowler's Report, p. 170) have been arranged into series. The stronger members of these series lie in the infrared and have not been observed. Two multiplets whose shortest wave-lengths are 1381.60 and 1473.00 respectively have been found in sulfur. They each contain the fundamental triplet differences and are attributed to a two electron transition. Strikingly similar groups have been found in chlorine which has lost an electron (Phys. Rev. 23, 766, 1924). The shortest wave-lengths of the triplets are 789.03, 834.83, 888.18, and that of the multiplet like the 1381 group of sulfur is 1063.88. By analogy with  $S_I$  the ionizing potential of  $Cl_{II}$  is provisionally calculated as 18.32 volts; hence that of  $Cl_I$  is about 9.16 volts.

7. **The quantum analysis of new nitrogen bands in the ultraviolet.** J. J. HOPFIELD and R. T. BIRGE, University of California.—A group of strong bands, degraded to the red, extending from  $\lambda 1354$  to  $\lambda 1854$ , appears in purified nitrogen, at 0.003mm pressure, arc discharge, using a long tube and flowing gas. The thirty observed bands (of which seventeen have previously been recorded by Lyman) have in general the customary intensity distribution and thus indicate definitely the correct assignment of vibrational quantum numbers. The resulting equation is  $\nu = 68,956.6 + (1681.45n' - 15.25n'^2) - (2345.16n'' - 14.445n''^2)$ , where  $n'$  varies from 0 to 3 only, and  $n''$  from 0 to 9. The average (obs.—calc.) is 0.1A. Contrary to expectations, the progressions occurring in this formula have no relation to any other analyzed group of bands, so that the chemical origin of the group is not definitely known. The usual nitrogen groups occur with great intensity on the spectrograms, and there are also a number of additional new bands (or at least hazy lines) between  $\lambda 950$  and  $\lambda 2100$ , but no consistent numerical relationships have as yet been found. Hence the hitherto assumed fundamental group of nitrogen bands in this region of the ultraviolet seems to be missing.

8. **The band spectra associated with carbon.** RAYMOND T. BIRGE, University of California.—Vibrational quantum numbers have, as far as possible, been assigned to all of the thirteen band groups associated with carbon, where such work has not already been done. It is found that the final states of the first negative group and of the comet-tail bands are identical, and both groups of bands are probably due to ionized CO. The intensity distribution in the comet-tail bands in a helium mixture, as observed by Merton and Johnson, is a low temperature distribution, in contrast with the high temperature distribution observed by Fowler and by Baldet. The high pressure CO bands have as a final state the initial state of the comet-tail bands, but more accurate measurements are needed for the former group. The triplet bands of Merton and Johnson have an intensity distribution similar to the comet-tail bands, and the final state may be the same as that of the third positive group, but the progression is too short to decide the question. The fourth positive group represents a remarkably slow initial vibration (500), and a very rapid final vibration (3000). No other new relations between progressions of these carbon groups or of others have been found.

9. **Emission from the Bunsen flame.** JOSEPH W. ELLIS, University of California, Southern Branch.—Using a new self-registering infrared spectrograph with two quartz prisms in Littrow mounting, the  $2.7\mu$  emission band of the Bunsen flame appears widely resolved with maxima at 2.58 and  $2.76\mu$ . A weaker doublet at 1.79, 1.99 and a still weaker broad band at 1.40 appear. These regions of emission correspond in general to numerous weak maxima found by Paschen in 1894 who identified them all except the long wave-



length part of the first mentioned band with water vapor since they also occur in the oxyhydrogen flame. Barker's assumption that the primary separation of the 2.7 carbon dioxide band is not a regular infrared doublet is here supported by the fact that a corresponding emission doublet would have a separation equal to that observed between the water vapor and carbon dioxide bands in this region. Calculation of the bunsen flame temperature from Barker's 4.4 emission and absorption doublet gives a value consistent with measurements.

**10. Secondary standards of wave-length in the spectra of neon and iron.** GEORGE S. MONK, University of Chicago.—A comparison has been made by the use of the interference spectrograph, of the wave-length of the primary standard obtained from a Michelson H-tube, an arc in vacuo, and a modified and brilliant form of tube. The results show the wave-length to be the same for all. Several neon lines recommended by the International Astronomical Union were compared with the primary standard from the new tube, giving a result of  $6438.4696 \pm 0.0003\text{\AA}$  for the primary standard, verifying the values of the chosen neon lines. Compilation of the results of nearly fifty observations show that the recommended values of two lines, 5852 and 5881, are questionable. In the spectrum of the standard ion arc, 110 lines have been compared with the spectrum of neon. While for lines shorter than 6000Å the results agree well with the last observations of the Bureau of Standards, in the red they are about 0.002Å lower. The values obtained for all the *b* lines are systematically lower for the Pfund arc than for the Bureau of Standards arc. Observational work done thus far on the vacuum iron arc leads to the belief that the adopted system of standards should be based on the arc at atmospheric pressure.

**11. The ionization of nitrogen as interpreted by positive ray analysis.** T. R. HOGNESS and E. G. LUNN, University of California.—The previously described method for the positive ray analysis of the products of electron-impact ionization of gases has been applied to nitrogen. Study of the relative intensities of the ions  $\text{N}_2^+$ ,  $\text{N}^+$  and  $\text{N}^{++}$  as a function of pressure gives evidence that in the ionization of nitrogen the primary process is the formation of  $\text{N}_2^+$ . The processes of ionization in nitrogen are thus analogous to those in hydrogen found by Dempster (Phil. Mag. 31, 438, 1916; Phys. Rev. 8, 651, 1916) and confirmed by Smyth (Phys. Rev. 25, 452, 1925) and by the authors (Phys. Rev. 25, 718, and 26, 45, 1925). The above conclusions are discussed in the light of the results of Smyth (Proc. Roy. Soc. 104A, 121, 1924, etc.)

**12. The energy of combination of gaseous ions.** J. H. HILDEBRAND, University of California.—The energy of combination of the gaseous ions of the alkali metals with the gaseous halide ions to form the solid halides have been calculated from the best available thermochemical and spectroscopic data. The values for the larger ions are about the same, approximately 165 kg cal., but they increase as the ions get smaller, becoming 233 with lithium fluoride. The figures approximate those of Born and Landé, although their assumptions are rejected in the light of criticisms by Latimer. The high values for the smaller ions are in harmony with their closer approach and greater contraction as shown from lattice constants. The affinity of a positive for a negative ion is related to but greater than its affinity for an electron; this explains the instability of monohalides of the alkaline earth metals with respect to metal and bihalide, in spite of the fact that the second ionization potentials of these metals are much greater than the first. The high energy values for the small ions likewise explain the abnormally high stability of compounds between the elements of low atomic number, many of which are not in harmony with familiar electrochemical criteria such as the "replacement series."

**13. Organic absorption media as color screens in the ultraviolet.** THOS. M. DAHM, University of Idaho.—Ultraviolet absorption spectra of aqueous solutions of organic compounds frequently show very broad deep bands on the edges of which the absorption coefficient  $\kappa$  approximates the curve  $\kappa = \kappa_1 e^{a(\nu - \nu_1)}$ . If such adjustment of concentration or of length of cell is made that the transmission  $I/I_0 (= e^{-\kappa c x})$  has a value less than  $e^{-1}$  for a spectrum line, the transmission of nearby lines will fall off more rapidly than  $\kappa$  rises. The "gradation constant"  $a = (1/\kappa) (d\kappa/d\nu = d(\log \kappa)/d\nu = -d(\log c)/d\nu$ . A geometrical series of decreasing concentrations will shift a given transmission from line to line in arithmetical series of frequencies; the medium can be used at any point in the range  $\nu - \nu_1$  by proper choice of  $c$  or  $x$ ; a choice of media can be made by comparing "gradation constants." Values of  $a$  have been found so large that adjacent strong lines of the mercury spectrum may be transmitted with 20 percent and less than 0.2 percent of the unabsorbed valued. Many substances transmit a characteristic high frequency band between broad absorption bands.

**14. Measurement of the light scattering coefficient of some saturated vapors.** SCOTT EWING, University of California.—This investigation is an attempt to verify the theory of light scattering by measuring the scattering coefficient and comparing it with the theoretical value which can be calculated from a knowledge of the compressibility and refractive index of the medium and the wave-length of the incident light. The saturated vapors of ether, benzol, chloroform, ethyl alcohol and methyl alcohol were used as scattering media. The effective wave-length of the incident light was calculated by measuring the effectiveness of the different wave-lengths of the source (a locomotive headlight) in blackening a photographic plate, and assuming that the scattering coefficient varies inversely as the fourth power of the wave-length, which is true except for the small effect of dispersion. The scattering coefficient was measured by making a photographic comparison of the intensity of the light scattered at right angles, with the incident intensity. The results agree with the theory within the limits of experimental error. The data may be used to make an estimate of the number of molecules per cubic centimeter and the result obtained is  $(2.68 \pm .04) \times 10^{19}$ .

**15. The reflecting powers of elements in the ultraviolet and the photo-electric thresholds.** RICHARD HAMER, University of Pittsburgh.—A comparison of the curves showing the reflecting power of different elements for different wave-lengths in the ultraviolet observed by E. O. Hulburt and of the reflection coefficients at different wave-lengths recorded in the Landolt-Bornstein tables 1923 with the observed photo-electric thresholds, reveals that there is a change in the reflecting power at a wave-length which coincides approximately with the threshold. This change of slope is sometimes quite marked and generally indicates that the reflecting power for shorter wave-lengths is decreased at this point. This indicates that energy is taken from the incident radiation and assists in bringing about release of photo-electrons from quantized orbits. Electrons in metals are not free but bound. In the following summarized examples the order of comparison is, approximate wave-length of change observed by Hulburt (H) or Hagen and Rubens (HR), the nearest observed threshold  $\lambda_0$  in brackets, and the author's predicted  $\lambda_0$  which equals the ionizing energy for some critical orbit  $I(x)$ : Cu (H) 3150, (HR) 2880, (3000),  $I(2p_1)$  3175; Ag, (H) 3383, (3390  $\pm$  60),  $I(2p_2)$  3383; Au, (H) 3010, (Meyer) 3010, (approx. 2850),  $I(2p_1)$  3010; Mg (H) 3750, (HR) 3800, (3820),  $I(2P)$  3750; Zn, (H) 3076, (Meyer) 3076, (3016),  $I(2P)$  3450; Al, (H) 3400, (3595  $\pm$  100); Sn, (H) 3200, (3185  $\pm$  55); Ni, (H) 3100, (HR) 2880, (3050  $\pm$  50); Pt, (H) 2900, (HR) 2749, (2780–35); Pb, (H) 3650, (3650); Sb (H) 3075, (3075); Bi, (H) 3068, (2980  $\pm$  50); W (H) 2635, (2615  $\pm$  30); Se (H) 2460, (2670  $\pm$  35); Fe 2850, (2870  $\pm$  40); Pd 2870, (approx. 2850).

16. "Raies ultimes" and photo-electric thresholds. RICHARD HAMER, University of Pittsburgh.—A comparative study of the energy values of the "raies ultimes" and the photo-electric thresholds as summarized in the following table points to the general rule that the photo-electric threshold (column 5) equals the difference between the ionization potential (column 4) and the energy (column 3) of a prominent "raie ultime" (column 2). On this basis the author is able to predict the ionization potentials and the corresponding terms or the thresholds for certain elements.

Element	Wave-length	Energy	Ionization	Threshold	Series term
Cu	3247 Å	3.80 v.	3.89 v.	4.11v.	$I_{(2p_1)}$
Ag	3281	3.76	3.78	$3.64 \pm .07$	$I_{(2p_1)}$
Au	2428	5.08	4.12	$4.33 \pm ?$	$I_{(2p_1)}$
Mg	2852	4.33	3.28	3.23	$I_{(2P)}$
Ca	4227	2.92	3.17	$3.08 \pm .16$	$I_{(2P)}$
Zn	2138	5.78	3.57	$3.60 \pm .08$	$I_{(2P)}$
Cd	2288	5.39	3.56	3.43	$I_{(2P)}$
Al	3961	3.12	2.84	2.58	$I_{(1s)}$
Tl	5350	2.26	3.82	$3.56 \pm .08$	$I_{(1s)}$
C	2479	4.98	....	$4.72 \pm .06$	....
Sn	3262	3.78	1.92	$3.87 \pm .07$	....
Pb	4058	3.04	4.35	$4.14 \pm .07$	....

17. On the thermo-electric properties of pure metals and alloys. A. E. CASWELL, University of Oregon.—Analyzing data used in the preparation of the International Critical Tables, the author shows that the thermo-e.m.f. between a compressed metal and the same metal when uncompressed, can generally be represented by an equation of the form  $E = apt(1 + bp)(1 + ct)$ . Exceptions are aluminum, iron and tin. Apparently aluminum undergoes a quasi-allotropic modification under pressures in excess of 6500 kg/cm<sup>2</sup>. The effect of pressure upon the concentration of free electrons in a metal is discussed. Changes in their thermo-electric properties as metals pass from the solid into the liquid are examined and deductions drawn therefrom on the basis of electron theory. The author also shows that in certain cases it is possible to predict the thermo-electric properties of an alloy from those of its constituents, especially when the pure metals unite in definite proportions, e.g. Ag-Pd alloys.

18. Parasitic thermo-electric forces in homogeneous metals due to a changing temperature gradient. E. D. MCALISTER, University of Oregon (introduced by W. P. Boynton).—When the ends of an apparently homogeneous wire are attached to a galvanometer and a Bunsen flame is used to heat a section of the wire to incandescence, no deflection is observed, unless the wire has been maltreated mechanically or is a non-homogeneous alloy. However, when the glowing part is caused to move along the wire by moving the flame, a current is observed to flow (large in the case of Fe and Ni), and the direction of the current is reversed when the direction of motion of the glowing part is reversed. Data on a considerable number of substances are presented and the relation to electron theory discussed.

19. Thermo-electric effects due to mechanical treatment; Benediks effect. L. J. NEUMAN, University of Oregon (introduced by Professor W. P. Boynton).—The end or central sections of annealed wires of Fe, Cu, Ni, Pb, Al, constantan, german silver, brass, nichrome, fuse wire and manganin were rolled, thus altering the crystalline structure. Thermo-electric powers as high as 2.6 microvolts per degree were obtained between the rolled and unrolled sections. The sign of the e.m.f. was not the same for different metals. Several experiments were carried out for each metal, all of which gave consistent results. In some cases the temperature vs. e.m.f. curve takes the form of a parabola. The e.m.f. from such a junction changes markedly with the amount of rolling and in some cases finally reached a maximum value and decreased. The influence of the length

of the transition section between the original and rolled portions has been studied but no consistent results secured. In all of this work pressure and soldered joints were eliminated because in many cases such contacts were found to produce e.m.f.s. of considerable magnitude. In some instances the thermo-electric properties produced by rolling are not completely eliminated by re-annealing the specimen. This seems to indicate the presence of a Benedicks effect; however results so far obtained are not sufficiently consistent to warrant definite conclusions.

**20. Thermal conductivity of some metals at high temperatures.** M. F. ANGELL, University of Idaho.—A continuation of some work done several years ago. The metal in form of a long hollow cylinder is heated electrically by a heavy current sent through it, the heat flow midway between the ends being assumed radial. The heat flow is calculated from resistance and current at a steady state. Temperatures are taken midway between the ends, upon the axis of the cylinder and at the surface, and thus the thermal conductivity determined. As temperatures inside and out differ only a few degrees and as the bar may be held at any temperature, complete curves are obtained for thermal conductivity from 50°C to the melting point. Data are given for aluminum, copper, nickel, and zinc.

**21. Extension of bar method of measuring specific heat.** MARCUS O'DAY, University of California.—Measurements of thermal and electrical properties of metals to be of theoretical value should all be made on the same sample under similar conditions or else all on single crystals. By sending a heavy current of proper magnitude through a bar whose ends are kept at zero temperature, electrical and thermal conductivities, their coefficients, and the Thomson effect can all be measured. By use of a double potentiometer, the thermo-electric power of the sample against the copper wire of the thermocouples can be measured. If the temperature of the middle of the bar is taken before the steady state is reached, the diffusivity is equal to  $[(2L)^2/\pi^2 t] \log [\theta_m/(\theta_m - \theta)]$  and the specific heat is equal to  $.00299\pi^2 I^2 R t / M \theta_m \log [\theta_m/(\theta_m - \theta)]$  where  $2L$  = length,  $R$  = resistance,  $M$  = mass of bar,  $\theta_m$  = temperature of middle at any time  $t$  measured from moment circuit is closed,  $\theta_m$  = value of  $\theta$  in the steady state, and  $I$  is proper value of current to compensate for heat loss. No difficulty attends the measurement of these quantities but appreciable error is introduced if the temperature of the ends changes. Corrections for this together with results of measurements of the above effects now in progress on Sn, Sb, and Zn will be published shortly.

**22. Design of an acoustic oscillograph.** S. H. ANDERSON, University of Washington.—An instrument has been designed of a purely mechanical type in which only the natural frequencies of the diaphragm on which the sound waves impinge need to be considered in the calibration, and hence a comparatively simple calibration curve is obtained. Diaphragms of mica, clamped at the edge, have been found to be the most satisfactory. In the investigation previously reported, the natural frequency of the first mode of vibration of diaphragms 5 cm in diameter seemed to be nearly independent of the thickness. Further work with carefully selected samples of different diameters and thickness shows that for a given diameter the natural frequency is a linear function of the thickness. Assuming Kennelly's equation  $2\pi n_0 = \sqrt{s/m}$ , the stiffness coefficient  $s$  is found to vary directly as the square of the thickness. The natural frequency is also a function of the diameter, increasing rapidly with a decrease of diameter. From this work it will be possible to predict the dimensions of a diaphragm for any specified frequency. It is desirable to select a diaphragm whose natural frequency is higher than that of any vibromotive force applied.

**23. The effect of reverberation upon the quality of speech.** VERN O. KNUDSEN, University of California, Southern Branch.—Speech articulation tests are being con-

ducted to determine the improvement in the quality of speech in auditoriums as a result of reducing the reverberation. The results obtained in several auditoriums, having approximately the same volumes and shapes but different times of reverberation, are tabulated below. The percentage articulation in each case, given in last three columns, is the average of observations made at essentially all parts of the auditorium.

Auditorium	Volume	Reverb.	Word art.	Vowel art.	Consonant art.
A	320,000ft <sup>3</sup>	7.5 sec.	44.0	88.0	65.4
B	280,000	5.3	56.3	92.0	73.0
C	310,000	5.0	64.5	97.0	79.0
B (corr.)	280,000	3.0	82.2	99.8	88.5
D	270,000	2.8	84.8	99.6	91.7

Tests in a room having a volume of 4096 ft<sup>3</sup> and a variable reverberation, controlled by bringing in different amounts of hairfelt, show that as the time of reverberation was reduced from 5.01 sec. to 0.60 sec., the word, vowel and consonant articulations increased, almost uniformly, from 51, 94 and 71 percent to 92, 99 and 96.5 percent respectively.

24. An anomalous sound absorption coefficient. S. H. ANDERSON, University of Washington.—The time of reverberation of sound in the auditorium of Anderson Hall (new Forestry Building) was found to be 70 percent of that required by the simple Sabine equation. The construction materials being the same as in rooms where the equation holds, an explanation was sought in the type of construction. The ceiling is supported by five steel trusses encased in wood, the crown of each truss being 16 feet below the peak of the ceiling. The apparent coefficient of absorption, ~~of the~~ wood covering the trusses, computed from the observed time of reverberation, was found to be 0.114, while the accepted value is 0.061. A reasonable explanation is that the mean free path of the sound waves is less and the number of reflections per second greater than in a simple room of the same volume, as the low hanging trusses divide the upper part of the room into six compartments. Sabine's exact equation  $t = (p/v)(1/a)\log[(p/v)(A/aVE)]$ , shows that  $t$  is a function of  $p/v$ , the number of reflections per second.

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THE  
PHYSICAL REVIEW

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## DIRECTED QUANTA OF SCATTERED X-RAYS

BY ARTHUR H. COMPTON AND ALFRED W. SIMON<sup>1</sup>

## ABSTRACT

Relation between the direction of a recoil electron and that of the scattered x-ray quantum.—It has been shown by cloud expansion experiments previously described, that for each recoil electron produced, an average of one quantum of x-ray energy is scattered by the air in the chamber. If the quantum of scattered x-rays produces a  $\beta$ -ray in the chamber, then a line drawn from the beginning of the recoil track to the beginning of the  $\beta$ -track gives the direction of the ray after scattering. Using a chamber 18 cm in diam. and 4 cm deep traversed by a carefully shielded narrow beam of homogeneous x-rays, with exploded tungsten wires as sources of light, nearly 1300 stereoscopic cloud expansion photographs were taken. Of the last 850 plates, 38 show both recoil tracks and  $\beta$ -tracks. The angles projected on the plane of the photographs were measured and it was found that in 18 cases, the direction of scattering is within  $20^\circ$  of that to be expected if the x-ray is scattered as a quantum so that energy and momentum are conserved during the interaction between the radiation and the recoil electron. This number 18 is four times the number which would have been observed if the energy of the scattered x-rays proceeded in spreading waves, that is if the direction of production of a  $\beta$ -ray was unrelated to the direction of the recoil track. The chance that this agreement with theory is accidental is about 1/250. The other 20  $\beta$ -rays are ascribed to stray x-rays and to radioactivity. This evidence seems a direct and conclusive proof that at least a large proportion of the scattered x-rays proceed in directed quanta of radiant energy.

AN increasingly large group of phenomena has recently been investigated which finds its simplest interpretation on the hypothesis of radiation quanta, proposed by Einstein to account for heat radiation and the photo-electric effect.<sup>2</sup> It has not been possible, however, to show that any of these phenomena necessarily demand this hypothesis for its explanation. Thus, for example, the photo-electric effect is not inconsistent with the view that the light energy proceeds from its source in expanding waves, if we postulate the existence within atoms of a

<sup>1</sup> National Research Fellow.

<sup>2</sup> An interesting summary of this work has been presented by K. K. Darrow in the *Bell Technical Journal* 4, 280 (1925).



mechanism for storing energy until a quantum has been received. It is true that no such mechanism is known; but until our knowledge of atomic structure is increased it would be premature to assert that such a storing mechanism cannot exist. The change of wave-length of x-rays when scattered and the existence of recoil electrons associated with scattered x-rays, it is true, appear to be inconsistent with the assumption that x-rays proceed in spreading waves if we retain the principle of the conservation of momentum.<sup>3</sup> Bohr, Kramers and Slater,<sup>4</sup> however, have shown that both these phenomena and the photo-electric effect may be reconciled with the view that radiation proceeds in spherical waves if the conservation of energy and momentum are interpreted as statistical principles.<sup>5</sup>

A study of the scattering of individual x-ray quanta and of the recoil electrons associated with them makes possible, however, what seems to be a crucial test between the two views of the nature of scattered x-rays.<sup>6</sup> On the idea of radiation quanta, each scattered quantum is deflected through some definite angle  $\phi$  from its incident direction, and the electron which deflects the quantum recoils at an angle  $\theta$  given by the relation<sup>7</sup>

$$\tan \frac{1}{2}\phi = -1/[(1+\alpha)\tan \theta], \quad (1)$$

where  $\alpha = h/mc\lambda$ . Thus a particular scattered quantum can produce an effect only in the direction determined at the moment it is scattered and predictable from the direction in which the recoiling electron proceeds. If, however, the scattered x-rays consist of spherical waves, they may produce effects in any direction whatever, and there should consequently be no correlation between the direction in which recoil electrons proceed and the directions in which the effects of the scattered x-rays are observed.

To make the test it is, of course, necessary to observe the individual recoil electrons and to detect the individual scattered quanta.<sup>8</sup> This we have done by means of a Wilson cloud expansion apparatus, in the manner shown diagrammatically in Fig. 1. In a recent statistical study,

<sup>3</sup> Cf A. H. Compton, *Jour. Franklin Inst.* **198**, 71 (1924).

<sup>4</sup> N. Bohr, H. A. Kramers and J. C. Slater, *Phil. Mag.* **47**, 785 (1924).

<sup>5</sup> It seems that there still remains a difficulty in accounting on this view for the intensity of scattered x-rays. See Y. H. Woo, *Phys. Rev.* **25**, 444 (1925).

<sup>6</sup> The possibility of such a test was suggested by W. F. G. Swann in conversation with Bohr and one of us in November 1923.

<sup>7</sup> Cf P. Deybe, *Phys. Zeits.* (Apr. 15, 1923); A. H. Compton and J. C. Hubbard, *Phys. Rev.* **23**, 444 (1924).

<sup>8</sup> A preliminary account of this work has been given in *Proc. Nat. Acad. Sci.* **11**, 303 (June, 1925).



we have found<sup>9</sup> that on the average there is produced about one recoil electron for each quantum of scattered x-rays. Each recoil electron produces a visible track, and occasionally a secondary track is produced by the scattered x-ray. When but one recoil electron appears on the same plate with the track due to the scattered rays, it is possible to tell at once whether the angles satisfy Eq. (1). If the photographs and the measurements can be made with sufficient definiteness, the experiment should thus give an unequivocal answer to the question whether the energy of a scattered x-ray quantum is distributed over a wide solid angle or proceeds in a definite direction.<sup>10</sup>

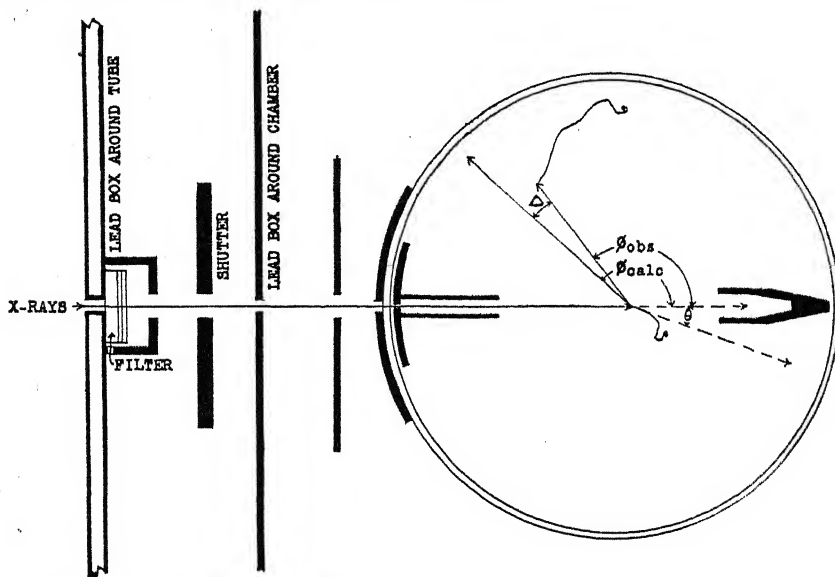


Fig. 1. Diagram of apparatus. On the hypothesis of radiation quanta, if a recoil electron is ejected at an angle  $\theta$ , the scattered quantum must proceed in a definite direction  $\phi_{calc}$ . In support of this view, many secondary  $\beta$ -ray tracks are found at angles  $\phi_{obs}$  for which  $\Delta$  is small.

*Experimental procedure.* In the final experiments we used a high voltage Coolidge x-ray tube excited by an unrectified alternating cur-

<sup>9</sup> A. H. Compton and A. W. Simon, Phys. Rev. **25**, 306 (1925).

<sup>10</sup> W. Bothe and H. Geiger have proposed (Zeits. f. Phys. **26**, 44, 1924) and carried out (Naturwissenschaften **20**, 440, May 15, 1925) a rather similar test. Using two point counters, one to receive the scattered x-rays and the other to receive the recoil electrons, they have found that many of the recoil electrons occur simultaneously with  $\beta$ -rays excited by the scattered x-rays. While such an experiment affords less definite evidence than does the present one regarding the directive nature of the scattered x-rays, it is equally incompatible with Bohr, Kramers and Slater's statistical view of the production of photo and recoil electrons.

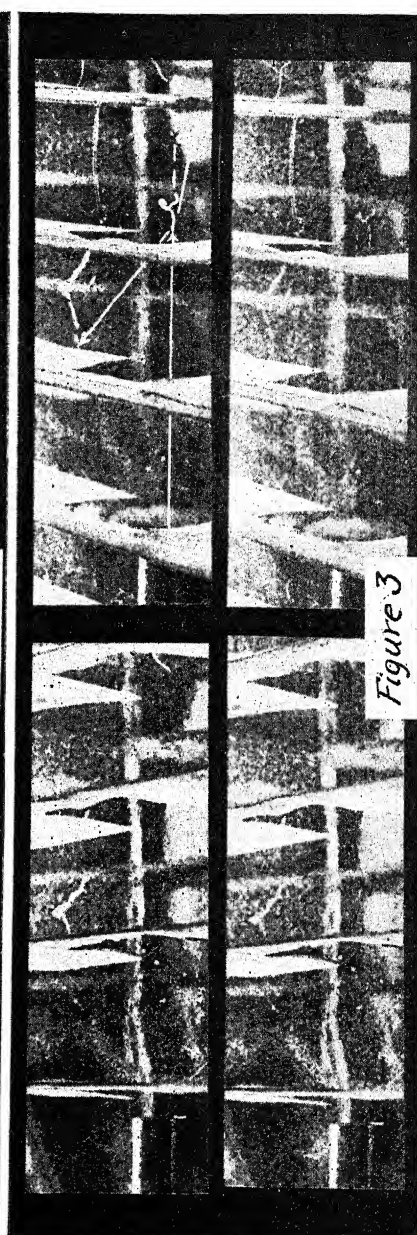
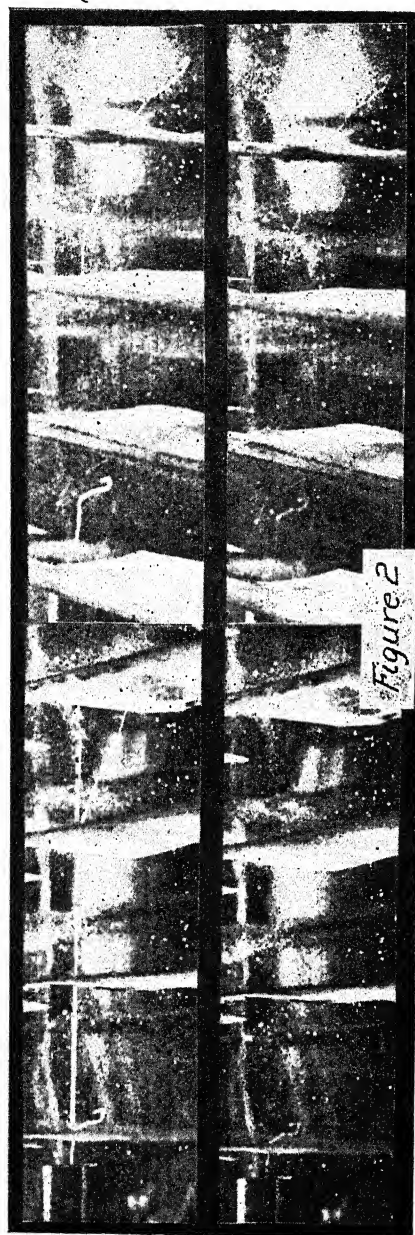


Fig. 2. A square hit. Plate 597. 1 recoil track, 1 secondary.  $\theta = -2^\circ$ ;  $\phi_{calc} = +175^\circ$ ;  $\phi_{obs} = +177^\circ$ ;  $\Delta = 2^\circ$ .  
 Fig. 3. Plate 560. 2 recoil tracks, 1 secondary.  $\theta = -25^\circ$ ;  $\phi_{calc} = +120^\circ$ ;  $\phi_{obs} = +120^\circ$ ;  $\Delta = 0^\circ$ . Recoil track (2) lies in wrong plane to be associated with secondary track.

rent at 140 peak kilovolts. Potentials as high as 250 kv were tried, but the resulting tracks of the recoil electrons were inconveniently long, and it was difficult to shield the expansion chamber adequately from the very penetrating direct rays. The x-rays were rendered approximately homogeneous by filtering through 6 mm of brass and about 2 mm each of copper and aluminium. Effects of stray x-rays were reduced to a minimum by surrounding the x-ray tube by a box of 9 mm lead, surrounding the expansion chamber with a box of 3 mm lead, and interposing suitable additional lead screens as shown diagrammatically in Fig. 1. The illumination was produced by exploding tungsten wires,<sup>11</sup> 0.1 mm in diameter and 14 cm long, by condenser discharges. The condenser, of about 0.1 microfarad capacity, was charged to about 70 kv by means of a separate transformer and "kenotron" thermionic rectifier. It was found necessary to surround this rectifier also with a box of 3 mm lead in order to avoid stray x-rays. The light entered the expansion chamber horizontally, at right angles to the primary beam, and the photographs were taken through the top of the expansion chamber in such a manner that the light was scattered by the water droplets at an angle of about 40°. We used an Ontoscope stereoscopic camera of 5.5 cm focal length, with the lenses stopped down to  $f/8$ . This gave ample exposure and a focus so deep that a  $\beta$ -ray track in any part of the chamber could be identified. Both the camera and the illuminating spark were enclosed within the lead box surrounding the expansion chamber.

In order to increase the probability that the scattered x-rays would produce  $\beta$ -ray tracks, a comparatively large chamber, about 18 cm in diameter by 4 cm high, was used. Diaphragms of thin lead foil were also suspended inside the chamber (see Figs. 2 to 5), so that the scattered x-rays might make themselves evident by ejecting photo-electrons. We allowed the primary rays to enter through a collimating lead tube, and absorbed them in a hollow lead cone. This eliminated almost completely the effect due to the scattering of the primary rays by the glass walls. When the expansion occurred, however, a slight blast of air proceeded from each of these lead tubes, and distorted the tracks for a distance of about 2 cm from the collimator and about 1 cm from the absorbing cone. It was accordingly possible to make accurate measure-

<sup>11</sup> The illumination obtained using the tungsten wires was roughly 10 times as brilliant photographically as that from a mercury spark at atmospheric pressure, using the same electrical energy.

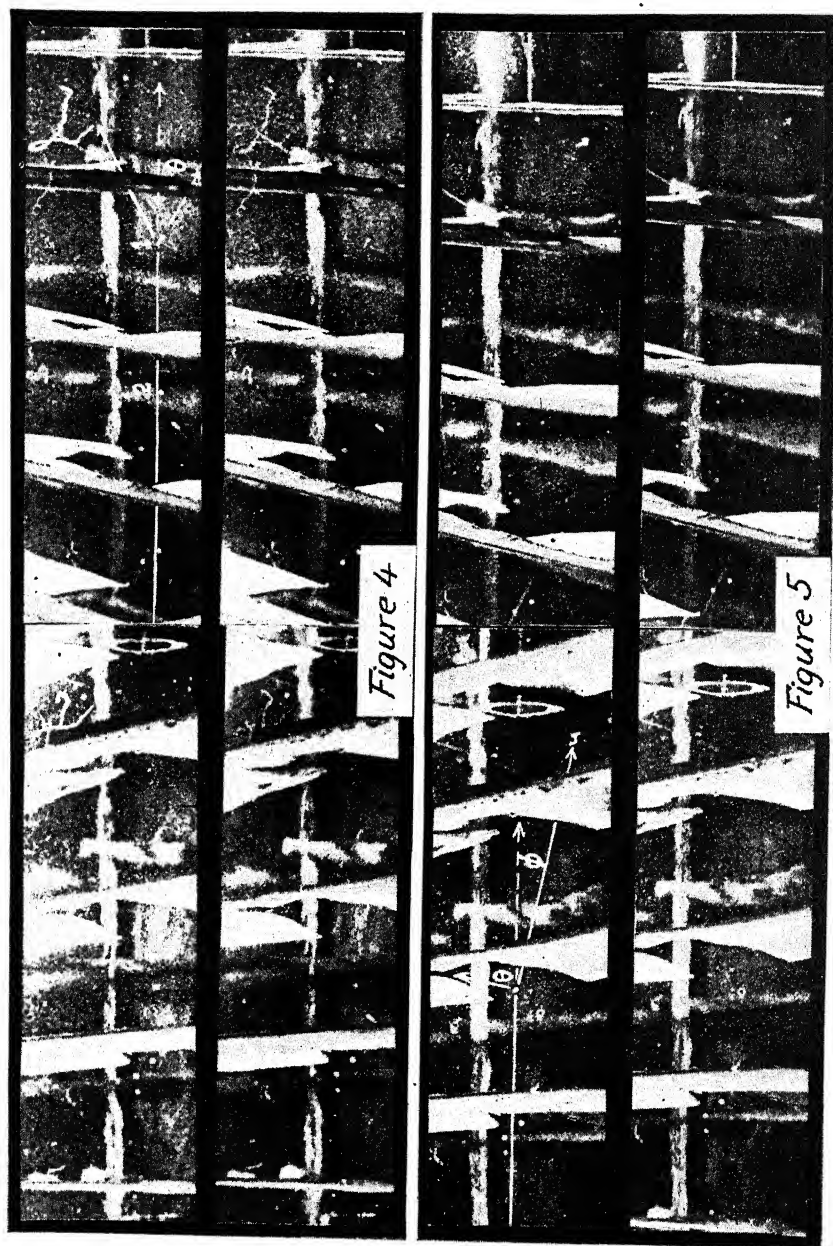


Fig. 4. Plate 1018. 2 recoil tracks, 1 secondary.  $\theta = -55^\circ$ ;  $\phi_{calc} = +59^\circ$ ,  $\phi_{obs} = +50^\circ$ ;  $\Delta = 9^\circ$ .  
 Fig. 5. A glancing blow. Plate 725. 1 recoil (sphere) track, 1 secondary.  $\theta = \pm 85^\circ$  as estimated from length of track;  
 $\phi_{calc} = \pm 8^\circ$ ,  $\phi_{obs} = -22^\circ$ ;  $\Delta = 14^\circ$  or  $30^\circ$ .

ments only on those recoil electrons which were ejected from a column of air about 4 cm long near the middle of the expansion chamber.

An examination of the photographs indicates that there was 1  $\beta$ -ray produced by x-rays scattered from this air column for about every 50 recoil electrons originating in this region, in satisfactory accord with a rough calculation based on the absorption coefficients of the x-rays and  $\beta$ -rays. There were in addition a considerable number of stray  $\beta$ -rays, due in part to stray x-rays and to radioactivity, as was shown by preventing the direct rays from entering the chamber, and probably in part also to the incompletely shielded scattered rays from the walls of the expansion chamber. The presence of these stray rays does not, however, present a serious difficulty in interpreting the photographs, since obviously there can be no correlation between their positions and the directions of ejection of the recoil electrons. Thus the effect of the scattered rays is a definite one superposed upon a random effect due to the stray  $\beta$ -rays.

*The photographs.* In making the preliminary adjustments and for auxiliary experiments we took about 140 photographs. The pictures which were useful in the final test were divided into three series. In the first series there were 302 plates. The second series of 338 plates and the third series of 511 plates were taken under improved conditions of x-ray shielding, thus reducing the number of stray  $\beta$ -ray tracks. There appear on the average two or three recoil tracks in each picture.

Typical photographs in which the secondary tracks appear are shown stereoscopically ( $\times 1.3$ ) in Figs. 2, 3, 4 and 5. In each case a retouched photograph with arrows marking the direction of the primary, recoil and scattered rays is placed above the untouched photograph. Unfortunately there appear on these plates also other marks due to water drops, pieces of lint, bubbles in the glass, etc. While these mar the beauty of the photographs, they do not impair their value, since such marks can always be identified by comparing successive plates.

*Analysis of the photographs.* An angular scale was placed on top of the expansion chamber and photographed with the camera raised half the height of the chamber. A transparency print of the resulting photograph was superposed on the negative of the tracks to be measured. By this means we measured the angles approximately as they would be projected on the plane of the top of the cylindrical chamber. We did not find it possible by means of the stereoscopic effect to make reliable estimates of angles in a plane including the line of sight. The



measurements were made on the original negatives, using a stereoscope with lenses of the same focal length as those of the camera.

When only one recoil electron and one secondary electron appeared on a photograph, the procedure was to record first the angle  $\theta$  at which the track of the recoil electron begins. The end representing the origin was rarely doubtful, since these tracks started within a narrow cylinder of air only about 1 mm in diameter. The angle between the incident ray and the line joining the origin of the recoil track and the origin of the secondary track was noted (when the origin of the secondary track

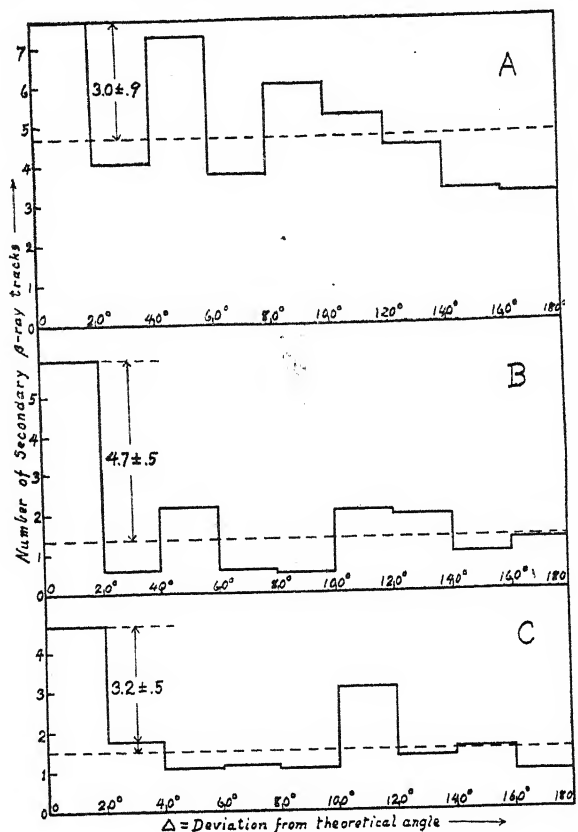


Fig. 6. The weighted number of secondary tracks at different angles  $\Delta$  from the theoretical position. The exceptionally large number between 0 and 20° indicates that many secondary tracks are due to rays scattered as directed quanta. Curve A: Some stray x-rays present. Curves B and C: Most of stray rays eliminated by lead screens.

could not be identified the measurement was made to a point midway between its two ends). The difference between this angle and the angle  $\phi$  calculated from  $\theta$  by equation (1) was called  $\Delta$ , and this value of  $\Delta$

was assigned a weight of unity. When a number  $n$  of recoil tracks appeared on the same plate with a secondary track, the value of  $\Delta$  was thus determined for each recoil track separately, and assigned a weight  $1/n$ . Following this procedure there are values of  $\Delta$  which are distributed approximately at random between 0 and  $180^\circ$  due to the  $n-1$  recoil electrons which are not associated with the secondary track. This is in addition to the random values of  $\Delta$  resulting from the presence of occasional stray tracks. We discarded the plates on which more than 3 recoil tracks appeared.

The results of this analysis are summarized in Figs. 6 and 7. Figure 6A shows the results for the first 302 plates, in which there appeared about 1 stray track for every 4 photographs. As will be seen, this was almost enough to hide the presence of the comparatively rare tracks due to scattered rays, which nevertheless show themselves by the exceptional concentration of  $\Delta$  values between 0 and  $20^\circ$ . Figs. 6B and

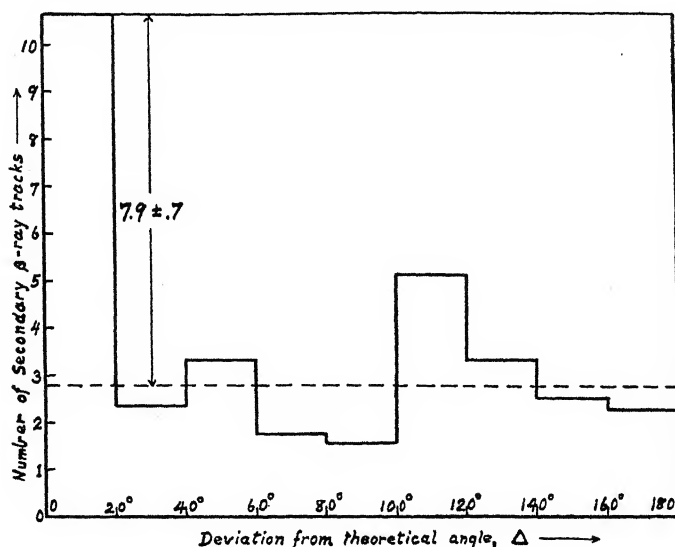


Fig. 7. Sum of curves 6B and 6C.

6C represent respectively the second and third series of plates, in which, by improving the lead shielding, the total number of secondary tracks was reduced to about 1 for every 20 plates. It will be seen that the result of this is to lower the general level of the random  $\Delta$  values and thus to exhibit much more prominently the concentration of these values at small angles. It is just such a concentration which is to be expected if Eq. (1) holds, that is if individual quanta are scattered in definite



directions from individual electrons. In Fig. 7 we have collected the results of the second and third series of plates. This figure shows the distribution of 38 secondary  $\beta$ -rays observed on these plates, 18 of which originate within  $20^\circ$  of the position anticipated from one of the recoil tracks present. The number 18 is about 4 times as many as would be expected if the distribution of the secondary tracks were a matter of chance. An idea of the degree of definiteness of the results can be obtained by calculating the probable variation from the mean of each of the 8 values between  $20^\circ$  and  $180^\circ$  by the usual formula,  $\pm .67\sqrt{\sum \delta^2 / (n-1)}$ , where  $\delta$  is the deviation of each value from the mean, and  $n$  is the number (8) of values. Thus we find that the number of pairs occurring with values of  $\Delta$  less than  $20^\circ$  is greater than the mean value for the other angles by  $7.9 \pm 0.7$ . The probability that so great an accidental deviation would occur in the positive direction is accordingly  $(1/2) \times (.7^2 / 7.9^2) = 1/250$ . It is thus highly improbable that so many pairs of tracks should as a matter of chance have been found to fit Eq. (1) satisfactorily.

Two other possibilities remain, (1) that the observed coincidences are the result of an unconscious tendency to estimate the angles falsely, making consistently favorable errors in measurement, and (2) that the agreement with Eq. (1) is real. Regarding the first possibility, we may note that using our methods of measurement it was hardly possible to make an error in determining the angle of ejection of the recoil electron of more than  $10^\circ$  nor in the angle at which the secondary electron appeared of more than  $5^\circ$ . It will be seen that errors of this magnitude could not alter the general form of the curve. The evidence therefore seems unescapable that Eq. (1) describes to a close approximation the angles at which many of the secondary electrons appear.

The question arises, does the presence in Fig. 7 of the considerable number of values of  $\Delta$  greater than  $20^\circ$  indicate the existence of scattered rays which do not obey the quantum law? It can be shown that about half of these random values of  $\Delta$  are to be expected merely from the fact that in most of the cases where Eq. (1) describes accurately the relation between the position of the secondary electron and the direction of motion of one recoil electron, there are one or two other recoil electrons which are in no way associated with the secondary  $\beta$ -ray. We are unable to assign definitely the origin of the remaining half of the random  $\Delta$  values. Undoubtedly some are due to stray x-rays which could not be completely eliminated and some are probably due to  $\beta$ -rays of radioactive origin. Our experiments cannot therefore be taken to

afford any evidence for the production of  $\beta$ -rays by scattered x-rays which do not conform to the quantum rule described by Eq. (1).

It is our conclusion, therefore, that at least a large part of the scattered x-rays under investigation produce  $\beta$ -rays at an angle connected by equation (1) with the angle of ejection of an associated recoil electron.

Since the only known effect of x-rays is the production of  $\beta$ -rays, and since the meaning of energy is the ability to produce an effect, our result means that there is scattered x-ray energy associated with each of these recoil electrons sufficient to produce a  $\beta$ -ray and proceeding in a direction determined at the moment of ejection of the recoil electron. In other words, at least a large part of the *scattered x-rays proceed in directed quanta of radiant energy*.

Since other experiments have shown that these scattered x-rays can be diffracted by crystals, and are thus subject to the usual laws of interference, there is no reason to suppose that other forms of radiant energy possess an essentially different structure. It thus becomes highly probable that all electromagnetic radiation is constituted of discrete quanta proceeding in definite directions. It is not impossible to express this result in terms of waves if we suppose that a wave train possessing a single quantum of energy can produce an effect only in a certain predetermined direction.

These results do not appear to be reconcilable with the view of the statistical production of recoil and photo-electrons proposed by Bohr, Kramers and Slater. They are, on the other hand, in direct support of the view that *energy and momentum are conserved during the interaction between radiation and individual electrons*.

RYERSON PHYSICAL LABORATORY,  
UNIVERSITY OF CHICAGO.  
June 23, 1925.

EXPERIMENTS ON THE WAVE-LENGTHS OF  
SCATTERED X-RAYSBY SAMUEL K. ALLISON<sup>1</sup> AND WILLIAM DUANE

## ABSTRACT

Intensity distribution of scattered x-rays as a function of wave-length.—(1) *Molybdenum rays*. Specially built tubes enabled the radiators to be placed only 1.6 cm from the target, so that reliable measurements were obtained from small radiators. An ionization spectrometer (methyl iodide) with a calcite crystal was used. For Li and Al, curves are given for various scattering angles. The results are similar to those obtained by previous observers for carbon, the shift of the maximum intensity of the modified band agreeing with the theory of A. H. Compton. Simultaneous irradiation by two x-ray tubes permitted scatterers to be employed that were small enough to allow a fairly accurate estimate of the *width of the modified band*. This width (for lithium) was thus found to be greater than that permitted by Compton's equation. The curves obtained show that the intensity of the unshifted line relative to the general radiation is less in the scattered spectrum than when obtained direct from the target of the tube. Less detailed experiments with Be, C, Na, NaCl, Mg and S are in agreement with the theory as far as shift is concerned and show that the relative intensity of the modified band decreases as atomic number increases. (2) *Tungsten rays*. In this case the radiator could not be placed nearer than 10 cm, so less reliable results were obtained. However the shifts are in general agreement with theory.

PRELIMINARY reports of these experiments have appeared elsewhere.<sup>2,3</sup> The experiments were performed with one of the ionization spectrometers in this laboratory which has been previously described.<sup>4,5</sup> The preliminary reports mentioned the use of special water-cooled x-ray tubes, similar to those first designed by A. H. Compton,<sup>6</sup> and of the multiple slits devised by Soller.<sup>7</sup> The water-cooled molybdenum targets in the special x-ray tubes were of the type furnished by the General Electric Company in the apparatus manufactured for experiments on x-ray diffraction. These targets were sealed into long, narrow, glass tubes constricted and made thin-walled in a region near the focal spot. With such tubes the scattering substance should be brought within 1.6 cm of the center of the focal spot. No great difficulty was experienced in evacuating these tubes

<sup>1</sup> National Research Fellow.

<sup>2</sup> Allison and Duane, Proc. Nat. Acad. Sci. 11, 25 (1925).

<sup>3</sup> Allison and Duane, Phys. Rev. 25, 235 (1925).

<sup>4</sup> Allison and Duane, J. Opt. Soc. Amer. and Rev. Sci. Inst. 8, 681 (1924).

<sup>5</sup> J. C. Hudson, *ibid.*, 9, 259 (1924).

<sup>6</sup> A. H. Compton, Phys. Rev. 22, 409 (1923).

<sup>7</sup> Soller, Phys. Rev. 23, 272 (1924).

so that they could be sealed off and run at 50 kv and 20 milliamp. from the high potential storage battery.

The multiple slits were constructed with 15 vanes of spring steel, 1 cm wide by 50 cm long, and .015 cm thick. These vanes were held between brass plates in which parallel grooves had been cut. Thus 14 parallel slits 50 cm long were produced, each slit .07 cm broad and 1 cm high. The calculated angular width of the beam from the slits was therefore 9.6 minutes of arc. The width of the unresolved Mo  $K\alpha$  doublet should then be 12.1 minutes of arc in the first order. The observed width agreed well with this calculation.

The composite beam from these slits was 1 cm wide and necessitated therefore a crystal face 8.7 cm long in order to reflect the whole beam at an angle of incidence of  $6^\circ 30'$ . (The critical angle of reflection of the Mo  $K\alpha_1$  line is  $6^\circ 43'$ .) An old face on a calcite crystal 9.2 cm long was finally adopted. This face was shown not to give spurious reflections by examining the Mo  $K\alpha$  lines direct from the target of the tube.

In the course of the work a set of curves was obtained which showed the change of wave-length of the modified radiation with scattering angle in the case of the scattering of molybdenum rays by lithium. Later these experiments were repeated with the beam defined only by two single slits and reflected from one of the crystals previously used for wave-length determinations in this laboratory. The curves obtained in this way confirmed completely the results from the multiple slits and large crystal, and also showed that the increase in intensity obtained by the use of multiple slits is really surprisingly small.

The gain in intensity due to the narrow x-ray tubes enabled us to use small radiators, or, what amounts to the same thing, to select for examination radiation from a portion of the scatterer in which the range of scattering angle is small. The importance of this has been previously considered,<sup>2</sup> and will be illustrated later.

In examining the scattering of molybdenum rays we have made more or less isolated experiments using scatterers of Be, C, Na, NaCl, Mg, and S. We have made more extensive studies of the scattering by Al and Li. The results confirm those of other experimenters who have published curves or photographs representing the scattering of Mo x-rays in a similar manner.<sup>8-12</sup> They show that in addition to scat-

<sup>8</sup> A. H. Compton, *Phys. Rev.* **21**, 483 (1923) et seq.

<sup>9</sup> P. A. Ross, *Proc. Nat. Acad. Sci.* **9**, 246 (1923) et seq.

<sup>10</sup> Compton and Woo, *Proc. Nat. Acad. Sci.* **10**, 271 (1924).

<sup>11</sup> J. A. Becker, *Proc. Nat. Acad. Sci.* **10**, 342 (1924).

<sup>12</sup> Kallman and Mark, *Naturwiss.* **14**, 299 (1925).

tered radiation having the same wave-length as the primary, as demanded by the classical theory of scattering, there is, at least for the light elements, a large portion of the scattered radiation which is shifted in wave-length and obeys the simple quantum theory advanced by A. H. Compton and independently by P. Debye. Recently curves have been obtained which show that there is an appreciable wave-length breadth of the shifted radiation, as announced by Compton,<sup>6</sup> which cannot all be accounted for by the range of the scattering angle. Such an effect has been theoretically treated by Jauncey<sup>13,14,15</sup> and ascribed to the binding of the electrons to the nucleus and their motion in the Bohr orbits in the atoms of the scattering substance.

The early, unpublished work by Bergen Davis and the photographs taken by Ross lead to the conclusion that the ratio of the intensity of the modified line to the unmodified decreases with increasing atomic number, and the experiments reported here support this conclusion.

The investigation of the scattering of molybdenum rays by heavy elements is made difficult by the extremely low intensity of the *scattered* radiation from these elements. Thus in our experiments on Mg and S, the intensity of the scattered radiation was so small that reliable curves were obtained only with great difficulty. This effect may perhaps be ascribed to the rapid increase of true or fluorescent absorption with rising atomic number, while by comparison the scattering per electron remains approximately constant.

The question of the variation in the intensity ratio of the modified to the unmodified line with angle of scattering for a given element and given incident wave-length has been theoretically investigated by Jauncey.<sup>14</sup> The experiments reported here unfortunately give no quantitative information on this interesting problem. Some experiments of Ross<sup>16</sup> seem to indicate that at small scattering angles the ratio of the modified to the unmodified line is decreased, and Compton<sup>6</sup> has also reported such an effect.

#### EXPERIMENTS WITH ALUMINIUM

The change of wave-length of the modified line with scattering angle is a fundamental part of the quantum theory of scattering advanced by A. H. Compton. Compton<sup>6</sup> has obtained curves showing this

<sup>13</sup> Jauncey, Phys. Rev. **24**, 204 (1924).

<sup>14</sup> Jauncey, Phil. Mag. **49**, 427 (1925).

<sup>15</sup> Jauncey, Phys. Rev. **25**, 314 (1925).

<sup>16</sup> Ross, Proc. Nat. Acad. Sci. **10**, 304 (1924).

effect in the scattering of Mo x-rays by carbon. In the present experiments a set of curves was obtained using aluminium radiators at various angles of scattering, and molybdenum primary rays. These are shown in Fig. 1. Simplified diagrams, showing to scale the relative positions

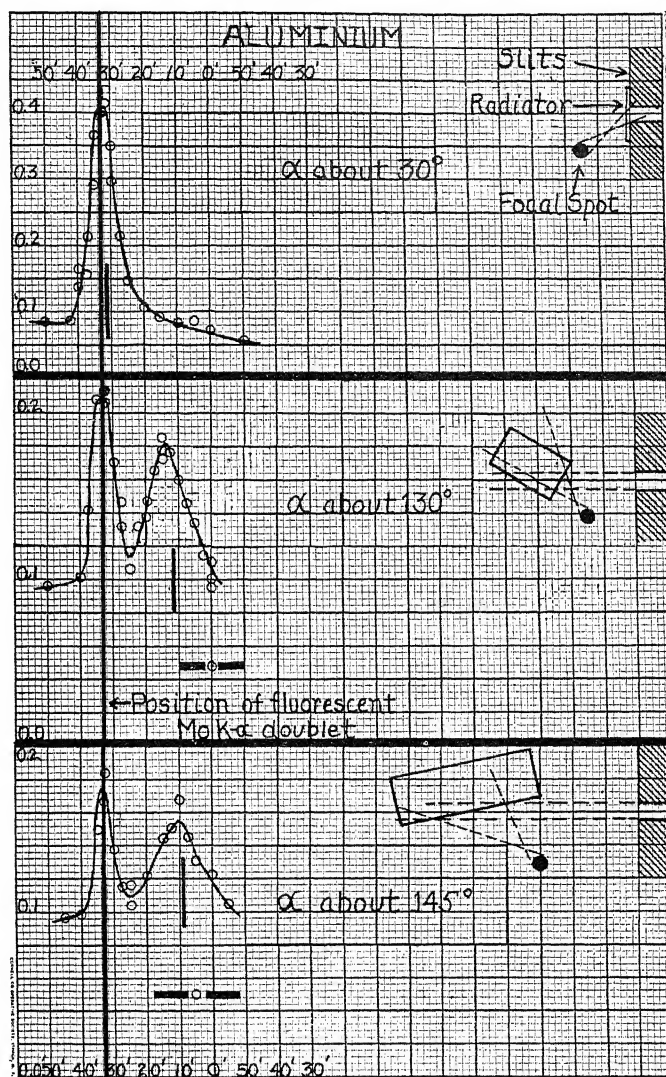


Fig. 1. Intensity distribution of x-rays scattered from Al at various angles.

and sizes of the scatterer, focal spot, and first slit appear at the right. The experiments were performed at a constant storage battery voltage



of about 40 kv and 20 m-amp. of current. The spectrometer scale was frequently calibrated by determining the position of the fluorescent molybdenum  $K\alpha$  doublet from a strip of molybdenum mounted in place of the scatterer. The position of this peak remained unchanged throughout the course of the experiments with aluminium and is indicated in the figure. The points below the curves taken at larger scattering angles show the ionization current obtained when the beam reflected by the crystal did not enter the ionization chamber slit. They therefore represent the height of the baseline due to natural leak of the electrical apparatus and to x-rays scattered by the crystal as an amorphous substance, etc. The position of the modified peak calculated from the Compton equation

$$\lambda - \lambda_0 = .0242 (1 - \cos \alpha)$$

is shown by a heavy vertical line in each case. Since the finite size of the focal spot and radiator made quite a range of scattering angles possible, the position of the modified line agrees within experimental error with that predicted by the quantum theory of scattering.

It may be demonstrated from these curves that the intensity of the unmodified line relative to the general radiation under it is less than in the case of the radiation from the target direct. This ratio depends on the slit widths and the voltage. From the central curve of Fig. 1 ( $\alpha = 130^\circ$ ) the value 3 to 1 may be calculated for this ratio. Spectra obtained from the target direct with the same slit width and voltage show that in this case the ratio is much greater, being about 18 to 1. The reason for this difference is not yet quite clear.

Fig. 2 shows the curve obtained when the range of scattering angle is large and includes the region about  $90^\circ$  where the wave-length of the modified line is changing most rapidly. Here every small volume of the radiator in the path of the slit is emitting an unmodified ray of constant wave-length, and a modified ray of a wave-length which depends on its scattering angle. Under these conditions, the theory indicates, and the experiment shows, that the shifted radiation is drawn out into a band whose intensity is low compared to that of the unmodified ray. This illustrates the difficulty in obtaining evidence of the Compton effect with large radiators.

In Fig. 2 and in every curve reproduced, *all* the readings of one experiment are plotted that were obtained in the angular range through which the curve extends. Due to mechanical or electrical disturbances of some kind, whose effects were appreciable relative to the very low



intensities in the spectrum of the scattered x-rays, readings were occasionally obtained (as in Fig. 2) which were difficult to include in a smooth curve. Such readings were repeated later, as is indicated by two or more points for the same angular setting, and almost invariably then gave values consistent with the general trend of the curve.

#### EXPERIMENTS WITH LITHIUM

A set of curves similar to those of Fig. 1, but with lithium as the scattering substance is shown in Fig. 3. The much greater intensity of the modified line with respect to the unmodified is at once apparent. These experiments were performed with two single slits defining the

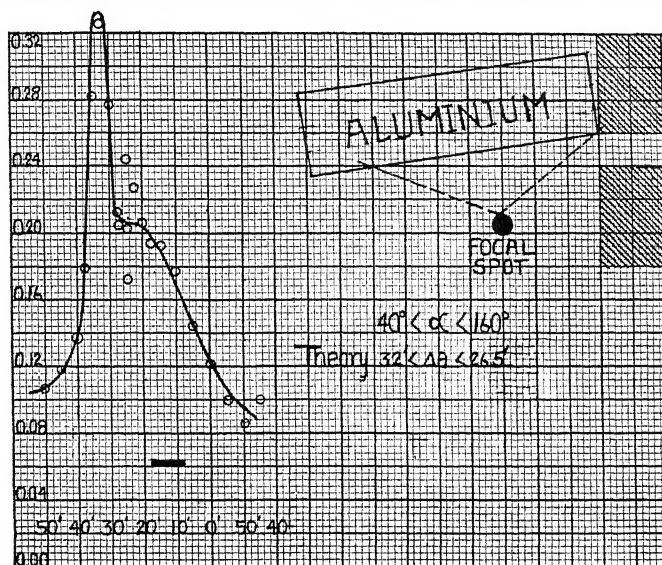


Fig. 2. Intensity distribution when the range of scattering angle is large.

beam. The results agree closely with those of similar experiments performed with multiple slits. With lithium as a scattering substance the intensity is much greater than with aluminium, and the curves, therefore, are more reliable. The lithium used appeared to be fairly free from oxide, and was kept coated with a paraffin oil during these experiments. The scattering from the carbon in this oil may have affected the relative intensity of the two lines somewhat. The slight shelf in the curve in which the angle of scattering is about  $100^\circ$  at the position of the unmodified peak was repeated several times and is undoubtedly present.

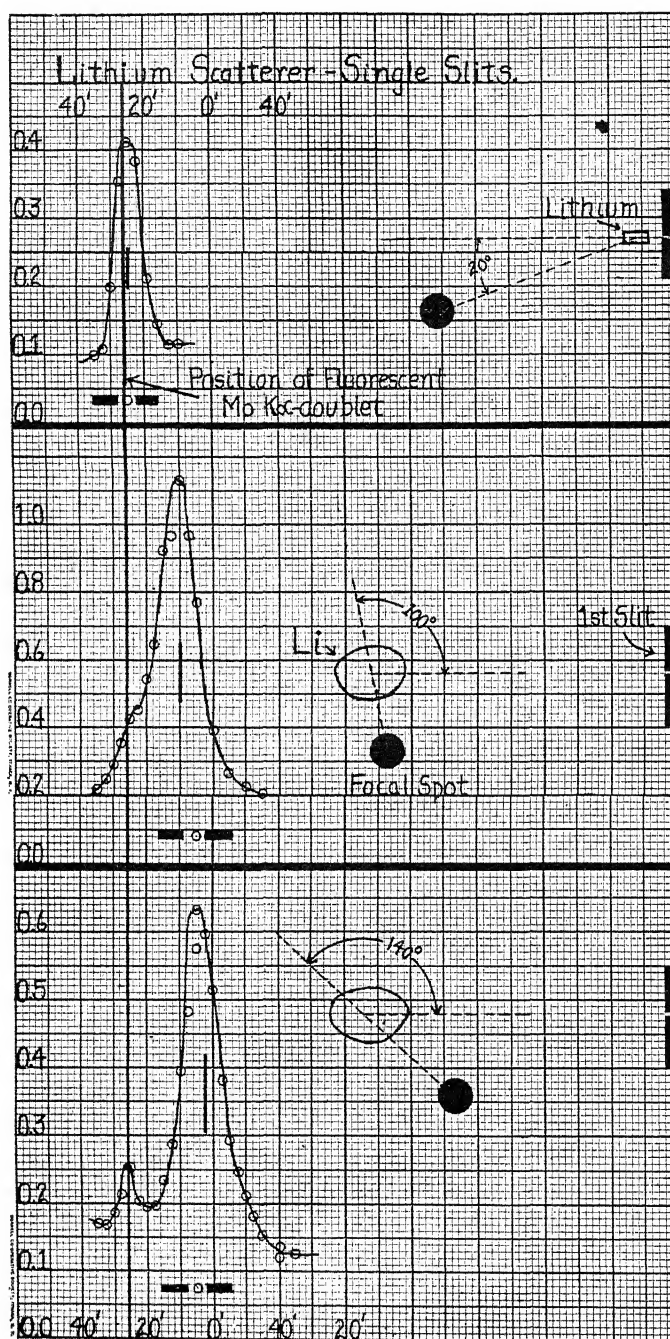


Fig. 3. Curves for scattering from lithium.

## EXPERIMENTS WITH TUNGSTEN PRIMARY RAYS

Spectrometer measurements on the scattering of tungsten rays have been reported by Compton<sup>6</sup> and by Ross.<sup>17</sup> Ross has found that the relative intensity of the modified line to the unmodified for a given element is much greater for tungsten rays than for molybdenum rays. M. de Broglie<sup>18</sup> has reported measurements of the Compton effect using tungsten primary rays.

We have not found it possible as yet to operate a narrow x-ray tube with a tungsten target at sufficient voltages to bring out the tungsten

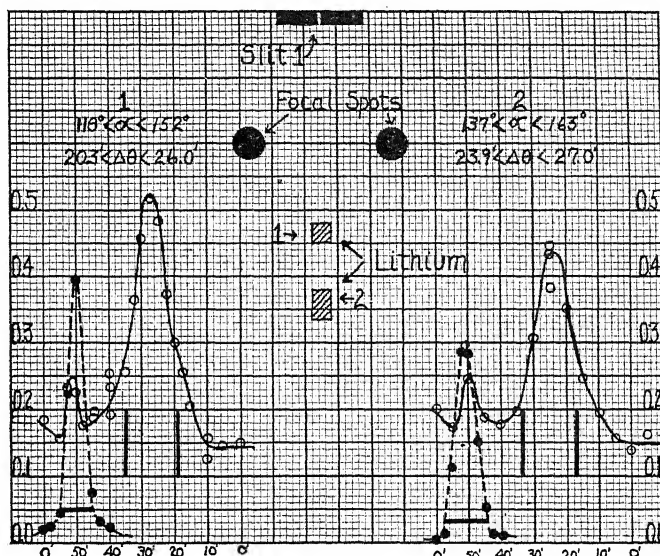


Fig. 4. Scattering from lithium irradiated from two Mo targets simultaneously.

characteristic rays strongly. Our experiments indicate that if this could be done, large intensities could be easily obtained. We have used a Universal type tube, operated at 100 kv and 6 m-amp. With this tube the radiators could not be placed nearer than 10 cm to the target. When the multiple slits were used, the rays were reflected internally from a thin slab of calcite placed across the beam. This solved the difficulty of obtaining a crystal long enough to take in the full beam by surface reflection at the small glancing angles involved. Aluminium and graphite radiators were used. The curves obtained were of low intensity, and not reliable as to details of shape, but showed

<sup>17</sup> Ross, Phys. Rev. 25, 235 (1925).

<sup>18</sup> De Broglie, Compt. Rend. 178, 908 (1924).

that the radiation was shifted as expected, and that the relative intensity of the shifted peak was greater for a given element than in the scattering of molybdenum rays, as reported by Ross.

#### THE BREADTH OF THE SHIFTED LINE

Experiments have been recently performed in which the radiator was irradiated from two molybdenum target tubes simultaneously. Some curves that have been obtained are shown in Fig. 4. The curve marked 1 was taken when each tube was running at 47.5 kv and 20 m-amp. from the storage battery. Curve 2 was taken at about 40 kv and the same currents. The relative positions of the tubes, radiator, and slit are shown on the diagram. Single slits were used. The diagram refers to a horizontal plane through the top of the slit, which was 2.5 cm high.

With the extra intensity supplied by the second tube, it was possible to use smaller radiators than before, from which we could make a good estimate of the maximum range of scattering angle possible. In making this estimate, we have assumed that the entire button of molybdenum in the target of the tube acted as a source of x-rays, and have taken account of the vertical dimension of the slit in calculating the minimum scattering angle possible.

The width of the slits was calibrated by taking the fluorescent radiation from a molybdenum plate. This is shown in dotted lines. The heavy lines at the base of the fluorescent peaks show the angular widths at which the excess intensity due to the characteristic lines has fallen to about 1/20th of its value at the maximum. From this width, and the minimum and maximum scattering angles permissible, the angular range in which the modified peak should rise and fall to 1/20th its value above the general radiation have been calculated from the simple Compton equation. These angular ranges are between the vertical lines underneath the modified peaks. It seems evident that the modified peak is broader than that predicted by the simple Compton theory, extending certainly to longer wave-lengths than Compton's equation permits. This effect is presumably connected with the binding of the electrons to the nucleus,<sup>13</sup> and therefore should be less marked in lithium than in other heavier elements. The high intensities obtainable from lithium, however, have made the use of this element desirable.

It appears on consideration that all the experiments reported here contain a slight element of uncertainty in view of the fact that methyl iodide was used in the ionization chamber and the second order of the

iodine critical ionization wave-length occurs in the region of the shifted peak from Mo  $K\alpha$ . This observation applies to all the experiments of previous observers in which ionization measurements were made with methyl iodide gas. The curves taken at small scattering angles (Fig. 1) indicate fairly well, however, that such an effect is practically negligible. The extent of the discontinuity introduced into the baseline depends on the fraction of the energy in the iodine critical absorption wave-length (.3737A) which is absorbed in the chamber. It is very much smaller in second order reflections than in first.

These experiments indicate that the shifted radiation should be considered to be a band with a sharp intensity maximum which obeys the laws deduced from the simple quantum theory of the scattering by free electrons. In any given atom, the rays scattered by the loosely bound electrons may be considered to give the modified radiation obeying more or less approximately the simple Compton equation. The rays scattered by the more firmly bound electrons may well produce the major part of the unmodified line and contribute most of the breadth of the shifted line in excess of that due to the range of scattering angle.

JEFFERSON PHYSICAL LABORATORY,  
HARVARD UNIVERSITY,  
Cambridge, Mass.  
May 26, 1925.



# SERIES SPECTRA OF TWO-VALENCE-ELECTRON ATOMS OF BORON ( $B_{II}$ ) AND CARBON ( $C_{III}$ )

BY I. S. BOWEN AND R. A. MILLIKAN

## ABSTRACT

Series spectra of  $B_{II}$  and  $C_{III}$ .—By methods previously reported in the identification of lines in the extreme ultraviolet, 13 lines in addition to the  $pp'$  group of  $B_{II}$  have been identified, completing the classification of all lines known to be due to  $B_{II}$ . Taking the  $4f$  level as 27800 (probably correct to within 200 frequency units), the following term values were obtained for  $B_{II}$ :  $3s$ , 72930.8;  $4s$ , 36655.5;  $2p_1$ , 165343.9;  $2p_{2,3}$ , 165362.7;  $3p_1$ , 59006.5;  $3p_{2,3}$ , 59010.0;  $3d$ , 52054.2;  $4d$ , 28640.4;  $5f$ , 17795.7;  $2S$ , 194325.9;  $3S$ , 66665.1;  $2P$ , 120929.4;  $3D$ , 48410.3. In the case of  $C_{III}$ , 8 lines in addition to the  $pp'$  group were identified, and taking the  $4f$  level as 62600, the following term values were obtained for  $C_{III}$ :  $3s$ , 146197.2;  $2p$ , 331939.2;  $3p_1$ , 124685.8;  $3p_2$ , 124698.6;  $3p_3$ , 124704.1;  $3d$ , 114387.2;  $2S$ , 375463.1;  $2P$ , 273111.0.

Progression of frequency separations and of screening constants for regular doublets for Li to O is shown in Table VI, for one to six valence electrons. The separation ( $2p_2 - 2p_1$ ) or ( $2p_3 - 2p_1$ ) regularly decreases and the constant  $s$  regularly increases, for a given element, with the number of valence electrons, irrespective of the fact that both doublets and triplets are involved.

## 1. IDENTIFICATION OF $B_{II}$ LINES

THE term-values of the stripped, or one-valence-electron, atoms of boron ( $B_{III}$ ) and carbon ( $C_{IV}$ ) have recently been worked out and published.<sup>1</sup> In the case of two-valence-electron atoms of these elements we have observed and published the characteristics of their  $pp'$  groups,<sup>2</sup> and have thus fixed with accuracy the frequency separations of the three  $2p$  levels, viz.  $2p_1$ ,  $2p_2$ ,  $2p_3$ .

But as soon as these separations are known it becomes possible to identify the boron lines which arise from jumps into these  $2p$  levels. Thus the separation between  $2p_1$  and  $2p_3$ , i. e., the total width of the triplet, is actually the distance between the second and the last components of the  $pp'$  group, numbering from the short wave-length side. This was found from the  $pp'$  plates to be  $22.8^{-1}$  for  $B_{II}$ .

The first member of the diffuse series of  $B_{II}$  ( $2p - 3d$ ) ought to be located at a wave-length a little larger than the corresponding line of stripped boron ( $B_{III}$ ) which was before found at  $\lambda\lambda 677.01$ ,  $677.16$ .

<sup>1</sup> Bowen and Millikan, Proc. Nat. Acad. 10, 199 (1924), and Nature 114, 380 (1924).

<sup>2</sup> Towne and Millikan, Phys. Rev. 26, 150 (Aug. 1925).

The only strong line on our plates in approximately this position is the line the wave-length of which we had published as 882.3A. In this region the foregoing separation would amount to but 0.18A. Since the  $p_2p_3$  separation was less than a third of this we could not hope to resolve all three of the  $(2p-3d)$  lines but could expect to obtain a resolution that would bring to light a doublet with a separation equal to the distance of  $p_1$  from the center of gravity of  $p_2$  and  $p_3$ .

We accordingly sought to obtain a spectrogram of the fifth and sixth orders of the line 882.3A. In both these orders it appeared as a doublet, as predicted, with a frequency separation of  $18.3\text{ cm}^{-1}$ . Since this is definitely different from the characteristic separations of both  $B_I$  and  $B_{III}$  it can only be due to  $B_{II}$ . Again, the  $(2p-3s)$  line of  $B_{II}$  must reveal the same separation as the foregoing but should have a slightly longer wave-length. Our next strong line, namely that at  $\lambda\lambda 1081.88, 1082.10$ , showed as a doublet in the fourth and fifth order spectra with a measured separation of  $19.3\text{ cm}^{-1}$ , in agreement within the limits of error with the foregoing.

The next jump most likely to occur is the  $(3d-4f)$ . This jump is between two remote circular orbits and its value may be computed roughly by multiplying the corresponding line for hydrogen by four. This gave  $\lambda 4688$ . The only unidentified line of any strength in this region was that at  $\lambda 4122.99$ , which was accordingly taken as the line sought.

The  $4f$  level for  $B_{II}$  would have a frequency value, if it were completely hydrogen-like, of  $109732/4 = 27433$ . The corresponding value for two-valence electron aluminum ( $Al_{II}$ ), which is certainly less perfectly screened than  $B_{II}$ , is 28440. The  $4f$  term-value for  $B_{II}$  had to lie between these limits and was taken as 27800, the uncertainty being not more than two or three hundred frequency units. With the aid of this starting point and the foregoing lines the  $3d$ ,  $2p$ , and  $3s$  levels were at once obtained as shown in Table I. The line  $(3s-3p)$  has not yet been observed, but a fairly accurate prediction as to its frequency can be made from the frequency of the corresponding line in  $C_{III}$  and the progression of the  $Mg_I$  to  $S_V$  series.<sup>3</sup> By taking this line as having a frequency 13920, the  $3p$  level was obtained from this frequency and the already-determined  $3s$  level. The jump  $(3p-4s)$  was found by looking for another doublet having the  $3p$  separations. This was found at  $\lambda\lambda 4473.37, 4474.08$ , and this fixed the  $4s$  level shown in the table.

<sup>3</sup> Bowen and Millikan, Phys. Rev. 25, 594 (1925).



The  $B_{II}$  singlet series was worked out as follows. By comparison with the  $3S-3P$  lines of the series  $MgI$  to  $Cl_{VI}$  and the already located  $2S-2P$  line of  $BeI$ ,<sup>4</sup> viz., 2348.70, it was seen that  $2S-2P$  for  $B_{II}$  should fall at about 1400Å. The only very strong line in this region, in fact the strongest unidentified boron line below 3000Å, was 1362.46Å. This could scarcely be any other than  $2S-2P$ . The next strongest

TABLE I  
Series lines for  $B_{II}$

Int.	$\lambda$ (I.A., vac.)	$\nu$	$\Delta\nu$	Term values
0	731.46	136712.9	$2p-4d$	$3s$ 72930.8
3	882.55	113308.2	$> 18.3$	$4s$ 36655.5
3	882.69	113289.9		
3	1081.88	92432.1	$> 19.3$	$2p_1$ 165343.9
3	1082.10	92412.8		$2p_{2,3}$ 165362.7
8	1362.46	73396.5	$2S-2P$	$3p_1$ 59006.5
3	1378.95	72519.1	$2P-3D$	$3p_{2,3}$ 59010.0
4	1623.66	61589.2	$pp'$ group	$3d$ 52054.2
4	1623.86	61581.7		$4d$ 28640.4
5	1624.08	61573.2		
4	1624.25	61567.0		$4f$ 27800.0
4	1624.46	61558.9		$5f$ 17795.7
5	1842.83	54264.3	$2P-3S$	
2	2918.98	34258.5	$3d-5f$	$2S$ 194325.9
10	3452.33	28965.9	$2S-2p_2$	$3S$ 66665.1
6	4122.99	24254.2	$3d-4f$	$2P$ 120929.4
1	4473.37	22354.5	$> 3.5$	
1	4474.08	22351.0		$3D$ 48410.3

lines to be expected were the  $(2P-3D)$  and the  $(2P-3S)$ , the former of which should have the shorter wave-length. The only unidentified boron lines below 3000Å, were<sup>5</sup> now  $\lambda 1378.95$  and  $\lambda 1842.83$ , the first of which should therefore be  $(2P-3D)$  and the second  $(2P-3S)$ . This fixes every known boron line of any strength except the familiar

<sup>4</sup> Paschen and Götze, *Seriengesetze* etc., p. 71.

<sup>5</sup> The line  $\lambda 1378.95$  did not appear in our original list of boron lines (*Phys. Rev.* 23, 7, 1924) because, with the resolution then used it was not separated from the strong aluminum line at  $\lambda 1379.7$ . With our present high-resolution the two lines are very easily seen to be distinct.

and exceedingly powerful line at  $\lambda_{vac} = 3452.33$  which, in conformity with the behavior of all two-valence electron systems is  $(2S - 2p_2)$ . This connects the singlet and triplet systems, the latter of which have been worked out above; i. e.  $2p_2$  being known, this last line fixes the value of  $2S$ , and from this all the other singlet levels come out at once from the foregoing relationships with the values given in Table I.

The present work then completes the identification of all the known boron lines of any intensity and the classification into series of all the lines due to B<sub>II</sub> and B<sub>III</sub>.

## 2. METHOD OF IDENTIFICATION OF C<sub>III</sub> LINES

One of the chief contributions of our development of hot-spark spectrometry to the identification of spectral lines has arisen from the fact that with these hot sparks we have been able to obtain for comparisons in the optical region a long series of atoms of varying nuclear charge but of like electronic structure and have found through such comparisons that such series follow the Moseley law quite as well in the field of optics as in the field of x-rays. The analytical expression of this law is

$$\frac{\nu}{R} = \left( \frac{Z - \sigma}{n} \right)^2 \quad (1)$$

in which  $\nu$  is the energy of the orbit expressed in terms of a frequency,  $Z$  the atomic number,  $\sigma$  the screening constant and  $n$  the total quantum number. We have already pointed out that the frequency  $\nu'$  of a spectral line due to an electron jump between two such orbits which have different screening constants  $\sigma_1$  and  $\sigma_2$  respectively must be given, with entire generality, by

$$\frac{\nu'}{R} = \left( \frac{Z - \sigma_1}{n_1} \right)^2 - \left( \frac{Z - \sigma_2}{n_2} \right)^2 \quad (2)$$

$$\text{or} \quad \frac{\nu'}{R} = \frac{(n_2^2 - n_1^2)Z^2 - 2(n_2^2\sigma_1 - n_1^2\sigma_2)Z + n_2^2\sigma_1^2 - n_1^2\sigma_2^2}{n_1^2 n_2^2} \quad (3)$$

an equation which shows, as previously pointed out, that when, and only when  $n_2$  is equal to  $n_1$  and  $\sigma_1$  and  $\sigma_2$  are independent of  $Z$ , do the frequencies  $\nu'$  progress linearly with atomic number  $Z$ , i. e., follow the irregular doublet law.

In seeking to use these relations for the prediction of the positions of the spectral lines of C<sub>III</sub> we observe first that the strongest C<sub>III</sub> line to be expected at all is the first term of the principal series of singlets,

viz.  $(2S-2P)$  and, since for this line  $n_2 = n_1$  and  $\sigma_1$  and  $\sigma_2$  may be expected to be independent of  $Z$ , there should be here a linear progression of  $\nu'$  frequencies with atomic number, a prediction which we have always found experimentally verified in the case of all lines that are due to jumps between orbits of the same total quantum number. Table II gives in its first two rows the frequencies of this line for two-valence-electron beryllium ( $\text{Be}_I$ ) and boron ( $\text{B}_{II}$ ) and enables us definitely to locate  $(2S-2P)$  for  $\text{C}_{III}$  at approximately  $73000 + 30000 = 103000$ , which corresponds to  $\lambda 971$ . This identifies the very strong carbon line 977.02 as the  $(2S-2P)$  line of  $\text{C}_{III}$ , for our plates taken with high resolution reveal this as the only singlet carbon line of any strength within a hundred angstroms of the predicted wave-length.

TABLE II  
*Irregular doublets,  $2S-2P$*

	Frequency	Diff.
$\text{Be}_I$	42565.1	
		30831.4
$\text{B}_{II}$	73396.5	
		28955.6
$\text{C}_{III}$	102352.1	

The next strongest  $\text{C}_{III}$  lines should be  $(2p-3d)$  and  $(2p-3s)$ . It is, however, impossible to locate them by means of the irregular doublet law, since,  $n_2$  being here different from  $n_1$ , this law can no longer hold. Eq. (3), however, is of general validity and gives the actual variation of  $\nu'$  with  $Z$  if only  $\sigma_1$  and  $\sigma_2$  are not functions of  $Z$ , as has been shown to be the case by the observed linear relation between  $\nu'$  and  $Z$  when  $n_1 = n_2$ .

Also (3) may be written

$$\nu' - RZ^2(n_2^2 - n_1^2)/n_1^2 n_2^2 = CZ + D \quad (4)$$

where  $C$  and  $D$  are constants so long as we are considering a given sort of electron-jump, i. e., a given set of values of  $n_2$ ,  $n_1$ ,  $\sigma_1$ , and  $\sigma_2$ . The quantity on the left will then show a linear progression with  $Z$ .

To transform this expression into one slightly more convenient for use we substitute  $(Z-A)$  for  $Z$  and get

$$\nu' - R(Z-A)^2(n_2^2 - n_1^2)/n_1^2 n_2^2 = C'Z + D' \quad (5)$$

The left side is again a quantity which varies linearly with  $Z$  and from which  $\nu'$  may be predicted for any value of  $Z$  as soon as any two other values have fixed  $C'$  and  $D'$ . For the case in hand  $n_2 = 3$ ,  $n_1 = 2$  and hence

$$R(n_2^2 - n_1^2)/n_1^2 n_2^2 = 109732(9-4)/[9 \times 4] = 15240.55 \quad (6)$$

We are here dealing with the progression with atomic number in the

frequency of a particular line found in the spectra of beryllium, boron, and carbon. Hence to make  $(Z-A)$  conveniently small we shall take  $A=3$ . Then with the use of Paschen and Götze's value of  $\nu'$  for  $2p_2-3d$  in beryllium (Be<sub>I</sub>) and our own value, determined above, of the same line in B<sub>II</sub> we obtain the first two numbers under column 2, Table III. The first two numbers of column 3 are obtained by subtracting 1 and 4 times 15240.55 respectively from these two frequencies in column 2. The numbers in column 3, which now represent the left side of Eq. (5), should progress linearly with  $Z$ , and hence the difference between them (first number in column 4) added to the second in column 3 should give the left side of Eq. (5) for C<sub>III</sub>. By adding  $9 \times 15240.55$  to this we obtain the frequency of  $2p-3d$  for C<sub>III</sub>. The result thus obtained is found to fall within 500 frequency units, or about 1 angstrom, of the strong carbon line at  $\lambda 459.7$ . The data given under C<sub>III</sub> in Table III are the *observed* values corresponding to this line and show how nearly linear is the actual progression.

TABLE III  
*Progression with atomic number of the frequency of  $(2p_2-3d)$  and  $(2p_2-3s)$*

		$\nu$	$\nu - (5/36)(Z-3)^2R$	Diff.
$2p_2-3d$	Be <sub>I</sub>	40075.13	24834.58	27511.42
	B <sub>II</sub>	113308.2	52346.0	28041.0
	C <sub>III</sub>	217552.	80387.	
$2p_2-3s$	Be <sub>I</sub>	30100.88	14860.33	16609.57
	B <sub>II</sub>	92432.1	31469.9	17107.1
	C <sub>III</sub>	185742.	48577.	

By precisely the same procedure, using the  $(2p-3s)$  frequencies for Be<sub>I</sub> and B<sub>II</sub>, we obtain the lower half of Table III and identify the strong carbon line  $\lambda 538.4$  as  $2p-3s$  for C<sub>III</sub>.

The next strong line to be sought in C<sub>III</sub> would naturally be  $(3d-4f)$  and since this is a jump between two fairly remote circular orbits it should be approximately hydrogen-like and hence have an approximate frequency 9 times, or a wave-length one-ninth of, the value for the corresponding line ( $\lambda 18751$ ) in hydrogen. The result is  $\lambda 2083$ , which identifies with sufficient accuracy the strong carbon line at 1930.98 as  $(3d-4f)$  for C<sub>III</sub>.

The carbon triplet at  $\lambda \lambda 4648.70, 4651.46, 4652.65$ , long ago found in the hottest stars (O type stars), obtained also in the laboratory by

Merton in 1915,<sup>6</sup> has already been classified as belonging to  $C_{III}$  because it does not appear in the arc spectrum, and, being a triplet, can therefore not belong to any stage of ionization of carbon other than  $C_{III}$ . It is here for the first time identified as  $3s-3p$  by the fact that its position is about right<sup>7</sup> for  $3s-3p$  and by the further fact that the separations of its components require it to be a line of a principal series and there is no other principal series triplet of suitable intensity.

The very strong carbon line at 2297.59 we identify as  $2S-2p_2$ , first by elimination—all of the other  $C_{III}$  lines that may be expected to be strong have already been identified and this line must belong to  $C_{III}$  since it is definitely a spark line and is not in Fowler's group of  $C_{II}$  lines; second, roughly by position—the  $2S-2p_2$  line in  $B_{II}$  being at  $\lambda 3452.33$ , the corresponding line in  $C_{III}$  may be expected to be somewhere between 2000 and 3000 Å; third, by its characteristics—this line comes out very easily for so high a stage of ionization and this is characteristic of the  $2S-2p_2$  line wherever it appears.

TABLE IV  
Series lines for  $C_{III}$

Int.	$\lambda$ (I.A., vac.)	$\nu$	$\Delta\nu$	Term values	
6	459.7	217552.	$2p-3d$	$3s$	146197.2
7	538.4	185742.	$2p-3s$	$2p$	331939.2
12	977.02	102352.1	$2S-2P$	$3p_1$	124685.8
4	1174.96	85109.0	$pp'$ group	$3p_2$	124698.6
4	1175.31	85084.2		$3p_3$	124704.1
5	1175.72	85054.0			
4	1176.03	85031.6			
4	1176.40	85005.1		$3d$	114387.2
7	1930.98	51787.2	$3d-4f$	$4f$	62600.
10	2297.59	43523.9	$2S-2p_2$		
3	4648.70	21511.4	$3s-3p_1$	$2S$	375463.1
2	4651.46	21498.6	$3s-3p_2$	$2P$	273111.0
1	4652.65	21493.1	$3s-3p_3$		

We have sought without success on our plates for the other singlet lines of  $C_{III}$  which might be expected to be strong, such, for example, as  $2P-3D$  and  $2P-3S$ . This failure might possibly raise some question

<sup>6</sup> Merton, Proc. Roy. Soc. 91, 498, (1915).

<sup>7</sup>  $(2p-3d) - (2p-3s) = 3s-3d = 31810$  (see above), and  $3s-3p$  should be about  $2/3$  of  $3s-3d = 21000 \text{ cm}^{-1}$  or at  $\lambda 4762$ .

about some of the other identifications, although it is in keeping with the fact that Fowler has been unable to find the corresponding lines in Si<sub>III</sub>.

The starting point for obtaining the series of C<sub>III</sub> levels from the foregoing lines was taken, as in the case of B<sub>II</sub>, as close to the theoretical hydrogen-like value for 4f. This hydrogen-like value for C<sub>III</sub> should be  $109732 \times (9/16) = 61724.3$ . We arbitrarily took, as in the case of B<sub>II</sub>, a value a trifle higher than this, namely 62600, and then obtained at once from this and the foregoing line-frequencies the term-values given in Table IV.

TABLE V  
*Comparison of term values*

	$\frac{N}{R/N^2} =$	2 27433.0	3 12192.3	4 6858.3
<i>s</i>	B/4	.....	18232.7	9163.9
	C/9	.....	16244.1	
<i>p<sub>1</sub></i>	B/4	41336.0	14751.6	
	C/9	36882.1	13854.0	
<i>d</i>	B/4	.....	13013.6	7160.1
	C/9	.....	12709.7	
	B/4	.....	.....	6950.
	C/9	.....	.....	6955.6
<i>S</i>	B/4	48581.5	16666.3	
	C/9	41718.1	.....	
<i>P</i>	B/4	30232.4	.....	
	C/9	30345.7	.....	
<i>D</i>	B/4	.....	12102.6	

Table V is added to conform with the general scheme of comparison of term-values that we have heretofore used, following Paschen and Fowler.

### 3. EFFECT UPON THE FORCE FIELD WITHIN THE ATOM OF THE SUCCESSIVE ADDITION OF ELECTRONS TO THE VALENCE SHELL

We have added a further Table VI for the sake of exhibiting even more strikingly than we have heretofore done, first, the systematic progression of the value of the screening constant *s* of the regular-doublet law as each new electron is added to the valence shell, and, second, the fact that the triplets behave precisely as do the doublets in systems of like electronic structure and varying nuclear charge.

The upper half of the table gives the  $(2p_2-2p_1)$  doublet-separations in the first, third, and fifth columns, for one, three, and five electron systems, respectively, and the  $(2p_3-2p_1)$  triplet separations in the second, fourth and sixth columns, for two, four, and six electron systems. For the two-valence electron systems these separations are obtained from the  $pp'$  groups. The lower half of the table gives the values of the screening constant  $s$  as computed from the regular doublet law as outlined in Physical Review 24, 209 (1924). The table shows very

TABLE VI

*Frequency separations and screening constants for regular doublets and triplets*

Electrons =	1	2	3	4	5	6
	$(2p_2-2p_1)$	$(2p_3-2p_1)$	$(2p_2-2p_1)$	$(2p_3-2p_1)$	$(2p_2-2p_1)$	$(2p_3-2p_1)$
Li	.338					
Be	6.61	3.02				
B	34.1	22.8	15.55			
C	107.4	79.1	66.76	46.8		
N	259.1	204.1	179.3	132.2	85.3	
O	.....	459.5	398.4	309.0	.....	224.0
Screening constant $s = Z - \sqrt[4]{\Delta\nu/.365}$						
Li	2.019					
Be	1.937	2.304				
B	1.884	2.189	2.445			
C	1.858	2.163	2.332	2.635		
N	1.838	2.137	2.292	2.638	3.090	
O	.....	2.043	2.252	2.606	.....	3.023

beautifully the effect upon the force-field about the nucleus of the successive addition up to six of each new valence electron to the valence shell. The progression is at least qualitatively quite such as is to be expected from the successive introduction into the atom of six point charges each endowed with a coulomb field.

NORMAN BRIDGE LABORATORY OF PHYSICS,  
CALIFORNIA INSTITUTE OF TECHNOLOGY,  
PASADENA.

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# THE ISOTOPE EFFECT IN BAND SPECTRA, IV: THE SPECTRUM OF SILICON NITRIDE

BY ROBERT S. MULLIKEN<sup>1</sup>

## ABSTRACT

**Silicon nitride bands.**—(1) A system of bands shaded toward the red, lying between 3800 and 5300 Å was obtained by Jevons in 1913 by the introduction of SiCl<sub>4</sub> vapor into active nitrogen. His measurements have been repeated and extended to all possible heads. It is important that no oxygen be present. From a sharp intense head each band decreases rapidly in intensity to zero at the null line, then increases to a maximum at about  $m = 13$  in the negative branch, in which the lines get far enough apart to be resolved. With the aid of the quantum theory, Jevons' arrangement was revised, and correct initial ( $n'$ ) and final ( $n''$ ) vibrational quantum numbers assigned. The null lines of the Si<sup>28</sup>N bands correspond to the wave-number equation:  $\nu^\circ = 24234.2 + 1016.30 n' - 17.77 n'^2 + 0.410 n'^4 - 0.00487 n' - 1145.00 n'' + 6.570 n''^2$ . Partial analysis of the band structure indicates that the lines of any band are given by the equation:  $\nu = \nu^\circ + B' + 2B'm + Cm^2$  where  $B' = 0.728 - 0.097n'$  and  $C = -0.0121 - 0.0097n' + 0.0053n''$ ; from this the internuclear distance for the vibrationless SiN molecule is  $1.56 \times 10^{-8}$  cm. Additional weak heads are present whose positions agree very closely with those calculated for the isotopes Si<sup>29</sup>N and Si<sup>30</sup>N, isotope 29 being slightly the stronger. This agreement definitely excludes SiO or any other compound than SiN as the emitter of the bands, confirming the chemical evidence. The agreement is also definite, but not conclusive, evidence against the existence of half-quantum numbers for SiN, a result opposite to that for BO. Plate I shows most of the Si<sup>28</sup>N bands together with some isotope heads. The intensity distribution in each band corresponds to thermal equilibrium at about 80°C. In respect to the initial vibrational quantum number, the distribution is non-thermal and corresponds to a high effective temperature as in other cases such as BO and CN. The intensity distribution with respect to  $\Delta n$  is similar to that of the violet CN bands. The sequence  $\Delta n = 0$  is by far the strongest, other sequences of diminishing intensity being observed as far as  $-3$  and  $+3$  or  $+4$ . (2) *New system of bands*, extensive but weak, probably also due to SiN, is described. They all have double heads ( $\Delta \nu = 27$ ), are shaded toward the red and extend from the ultraviolet through the green. An equation for the heads is given. The intensity distribution is characterized by numerically large values of  $\Delta n$  and by the absence of the band ( $0 \rightarrow 0$ ) and some neighboring bands.

## INTRODUCTION

IN 1913 Jevons described<sup>2</sup> an interesting band spectrum obtained by the introduction of silicon tetrachloride vapor into active nitrogen, and consisting in a system of bands, shaded toward the red, lying in

<sup>1</sup> National Research Fellow.

<sup>2</sup> W. Jevons, Roy. Soc. Proc. 89A, 187 (1913-14).

the region between  $\lambda 3800$  and about  $\lambda 5300$ . Jevons ascribed the bands to a nitride of silicon, this being supported by the fact that they were not obtained by the discharge through pure  $\text{SiCl}_4$  and by the further fact that a nitrogen-containing product was deposited on the walls of the nitrogen afterglow tube during the emission of the bands. As Jevons pointed out, the action of active nitrogen on  $\text{SiCl}_4$  is similar to its action on carbon compounds, the cyanogen bands being emitted in the latter case. Many of the bands, according to Jevons, show a minimum of intensity about  $4A$  from the head, a similar phenomenon being observed in the cyanogen bands when produced in active nitrogen. Jevons arranged all the bands in rows and columns such that the successive intervals of frequency taken vertically and horizontally form arithmetical progressions (the intervals being substantially constant in a given row or column of frequency-intervals), and from these he determined the constants of a Deslandres equation.

In addition to the data on the heads of the silicon nitride bands, Jevons gives a list of silicon lines which are emitted at the same time. In the present work, one additional Si line was found, that at  $\lambda 4103.1$ , and possible indications of one or two others.

In the light of the quantum theory of band spectra, it is now evident that the intensity minimum observed by Jevons in many of the bands must represent the region of the null-line, or missing line, which is of much more importance from a theoretical standpoint than the usually much more obvious head. The unusual prominence of the null-line here must be ascribed to the low temperature of active nitrogen; this subject has been discussed by Birge in the analogous case of the cyanogen bands.<sup>3</sup> The null-lines are plainly visible in two of the bands in Jevons' reproductions, and are particularly well brought out in photographs taken by the present writer (cf Plate I). The structure of the bands is of a simple type (probably like that of the violet cyanogen bands) which in the light of the quantum theory, shows that they are due to a diatomic emitter. That they are due to the compound  $\text{SiN}$  is probable from the chemical evidence (including that above cited and new evidence given below), and is definitely proved by the isotope effect (see below).

A re-examination of the silicon nitride spectrum was undertaken by the writer in 1923 with the object of studying the expected isotope effect. At this time Si was known from Aston's positive ray work<sup>4</sup>

<sup>3</sup> R. T. Birge, *Astrophys. J.* 55, 273 (1922).

<sup>4</sup> F. W. Aston, *Isotopes*, 2nd ed. p. 77 (1924).

to contain a small amount of an isotope 29 in addition to the dominant isotope 28; there was also doubtful evidence of an isotope 30 in small amounts, the doubt being occasioned by the possible presence of H compounds of the same mass-number. Jevons' data on the SiN bands evidently refer to  $\text{Si}^{28}\text{N}$  heads, and include no measurements which can be attributed to  $\text{Si}^{29}\text{N}$  or  $\text{Si}^{30}\text{N}$  heads. New photographs by the writer showed clearly, however, that each favorably located  $\text{Si}^{28}\text{N}$  head of sufficient intensity is accompanied by two approximately equally spaced weak satellites at the theoretically expected positions for  $\text{Si}^{29}\text{N}$  and  $\text{Si}^{30}\text{N}$ , isotope 29 appearing to be slightly more abundant than isotope 30. This was reported in a letter to Nature.<sup>5</sup> The existence of isotope 30 was later confirmed by Aston by the positive ray method,<sup>6</sup> it being found slightly less abundant than 29, in agreement with the results on the SiN bands.

In order to determine the theoretical positions of the isotope heads, vibrational quantum numbers were assigned to the bands measured by Jevons, making use of the latter's arrangement of the bands in rows and columns, and merely changing his empirical numbers  $m=22, 21, \dots, 12$  and  $p=55, 54, \dots, 50$ , to  $n'=0, 1, \dots, 10$  and  $n''=0, 1, \dots, 5$ ,  $n'$  being the vibrational quantum number of the initial electronic state of the molecule,  $n''$  that of the final state. Measurements were also made on the null-lines, using Jevons' measurements on the heads as reference standards, and an equation for the null-lines in terms of  $n'$  and  $n''$  was obtained.<sup>7</sup> On this basis, the isotope effect showed good agreement with theory for the final state of the molecule but was abnormally large for the initial state, especially for large values of  $n'$ ; this anomaly was associated with various other peculiarities for the initial state, in particular with an extraordinary low vibration frequency as compared with that of the final state.<sup>5,7</sup> Complete new measurements of the heads and null-lines of the SiN bands were recently made, in order to be more certain as to the reality of the abnormal isotope effect, and in order if possible to find a means of avoiding it. With the new data, which differ considerably from those of Jevons in a few cases, the above arrangement of the bands in rows and columns now gives rather small, but definite and systematic, deviations from the constancy required by the combination principle for the frequency-intervals between neighboring rows, or neighboring

<sup>5</sup> R. S. Mulliken, *Nature*, March 22, 1924.

<sup>6</sup> F. W. Aston, *Nature*, Aug. 23, 1924.

<sup>7</sup> Paper presented before Am. Phys. Soc.; abstract in *Phys. Rev.* 23, 554 (1924).

columns. By an arrangement of the bands differing radically from the old, it is found possible to satisfy completely the requirements of the combination principle and thus be sure that the new assignment of vibrational quantum numbers is correct. With this assignment, all the previous peculiarities and anomalies disappear and the isotope effect, in particular, is found to be in complete agreement with the theory. The former plausible but incorrect assignment is now seen to have been due to an unusual combination of misleading circumstances and relations. For the *heads*, it may be noted, the constancy of the frequency intervals is better with the old assignment; but this is of course of no theoretical importance.

#### EXPERIMENTAL PROCEDURE IN PRODUCTION AND MEASUREMENT OF BANDS

*Production of bands; evidence on nature of emitter.* The bands were obtained by the same general method as that of Jevons, using active nitrogen. In the latter part of the work, the same apparatus was used as in the work on the copper halide bands,<sup>8</sup> except that the bulb containing the silicon chloride, instead of being heated as in the case of the copper salts, was separated from the afterglow tube by a stopcock to control the flow of  $\text{SiCl}_4$  vapor,  $\text{SiCl}_4$  being a very volatile liquid. The  $\text{SiCl}_4$  used was some material, free from  $\text{CCl}_4$  in particular, which had been especially purified in connection with atomic weight work and which was kindly made available by Professor G. P. Baxter.

As noted in a previous paper,<sup>9</sup> the purple glow of the  $\text{SiN}$  bands is obtained in good intensity only when the nitrogen used is very free from oxygen, this behavior being in marked contrast to that of the  $\text{BO}$  bands and constituting strong evidence for the nitride origin of the present bands. Photographs were taken of an arc between silicon electrodes in an atmosphere of nitrogen in the hope of finding the  $\text{SiN}$  bands and getting additional evidence as to their nitride origin; but they were not present, perhaps because of a trace of oxygen impurity. The silicon arc in air gives oxide bands.<sup>10</sup> Apparently at high tem-

<sup>8</sup> R. S. Mulliken, *Phys. Rev.* **26**, p. 1 (July, 1925); cf. Fig. 1 and p. 7-8.

<sup>9</sup> R. S. Mulliken, *Phys. Rev.* **25**, 259-94 (1925). See p. 277.

<sup>10</sup> A. del Campo, *An. Soc. Esp. de Fis. Quim.* **13**, 98 (1913); A. del Campo and J. Estalella, *ibid* **20**, 586 (1922); C. Porlezza, *Atti. accad. Lincei* **31** (ii) 513 (1922), and *Gazz. Chim. Ital.* **53**, 215 (1923); W. Jevons, *Roy. Soc. Proc.* **106A**, 174 (1924). The bands, which are those of a diatomic emitter, are in all probability due to  $\text{SiO}$ , since the presence of oxygen is required (del Campo, Jevons). The heads can be represented by the equation (cf R. Mecke, *Phys. Zeit.* **26**, 239, 1925)  $\nu = 42,643 + 844.5 \nu' - 5.8 \nu'^2 - 1236.0 \nu'' + 6.04 \nu''^2$ .

peratures the affinity of silicon for oxygen exceeds that for nitrogen, while the fact that the carbon arc in air gives the CN bands indicates that the reverse is true for carbon.

*New photographs and measurements.* The photographs were obtained with the Hilger glass prism spectrograph used in previous work on BO and CuI, and all precautions were taken to secure the best possible definition. Greatly enlarged reproductions from one of the photographs are shown in Plate I. For the measurements, three photographs were used with a copper arc and three others with an iron arc comparison spectrum. Detailed measurements were made on one of these, and enough measurements on the others to make sure that they all gave consistent results, showing the absence of appreciable displacements in the comparison spectra. As in the case of the BO bands,<sup>11</sup> the results differed appreciably from those of Jevons, being consistently lower by 2–3 wave-number units in the region from  $\lambda 3950$  to  $\lambda 4360$ , but differing irregularly in the region of longer wave-lengths, being for the most part a few or even several units higher. For the weaker bands, these differences may be ascribed to inaccuracy in Jevons' measurements, in accordance with his statement that the accuracy is low for these bands. The consistently lower present results in the short-wave-length region of stronger bands are more difficult to explain. In the case of BO, it was suggested that such a difference might arise if in Jevons' measurements the setting was made on the extreme high-frequency edge of the head, while in those of the writer it was made at the point of maximum blackening, the heads being treated like lines. A comparison of the two methods of setting for a number of the SiN bands gave an average difference for the two methods of about 0.010 mm, the difference being surprisingly constant for bands of greatly varying intensity and structure. Since this difference corresponds to an average of only about 1.1 wave-units with the dispersion used, the suggested explanation is evidently inadequate to account for the discrepancy between the present results and those of Jevons. No further attempts have been made to determine the cause of the discrepancy, since a possible small constant error is obviously of minor importance in the theoretical interpretation of the data. The data on heads given in the following tables were all obtained by the method of setting on the point of maximum blackening for each head.

Measurements were made on the heads of all possible Si<sup>28</sup>N bands. The ultraviolet was photographed with a quartz spectrograph, in order

<sup>11</sup> Mulliken, loc. cit.<sup>9</sup>, p. 267-8.

## DESCRIPTION OF PLATE I.

Beginning with the top row, the reproductions show the entire SiN spectrum between  $\lambda 3986$  and  $\lambda 4800$ . They were made in four sections from a single negative; each junction point is indicated by a dot *above*; in each successive section a somewhat more heavily exposed print was used than for its neighbor to the left in order to show both strong and weak heads to best advantage. Except for this (and an undue weakening of the bands at the high-frequency end due to prism absorption, and of the 7,9 band at the other end by decreasing plate sensitivity) the reproduction gives an essentially correct idea of the intensity distribution.

The *head* of each  $A$  band of  $\text{Si}^{28}\text{N}$  is marked with a line, and the vibrational quantum numbers ( $n'$ ,  $n''$ ) are given. In the case of the more intense bands, the fall of intensity from the head to the null-line, and the rise to a maximum in the negative branch before the final fading out, are well shown. The weak  $\text{Si}^{29}\text{N}$  and  $\text{Si}^{30}\text{N}$  heads, which are at the left of the corresponding  $\text{Si}^{28}\text{N}$  heads, are marked when visible. The pairs of dots under the lowest section of the plate indicate the positions of the heads of some of the *new* bands; beginning at the left, the (1,5), (0,5), (1,6), and (2,7) head-pairs are marked; of these (1,5) is the most clearly visible. Unmarked conspicuous heads or lines (aside from structure lines of the bands) are of unknown origin (cf Table VI).



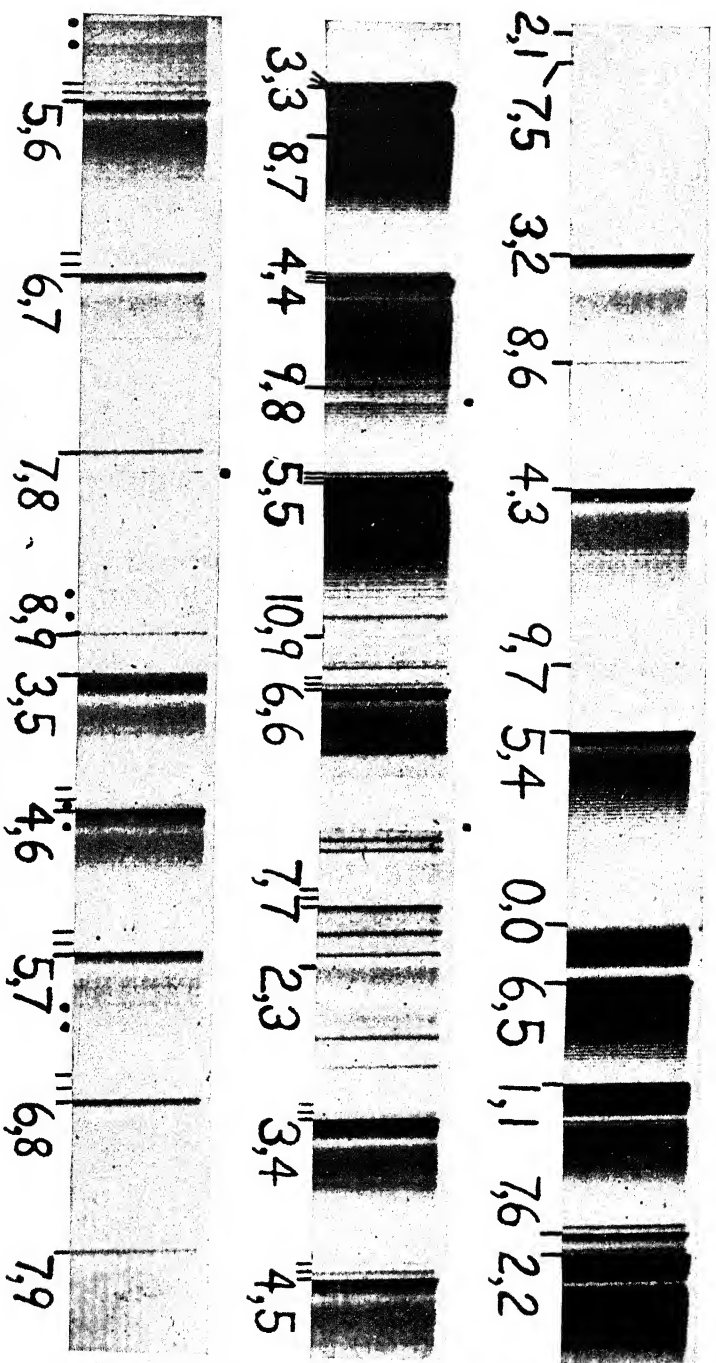


PLATE I. The entire band spectrum of SiN from  $\lambda 3086$  (top) to  $\lambda 4800$  (bottom).





to measure a few heads which were not transmitted by the glass prism. Some new bands of a different type were also found; other new bands were also found in the green (see later section).

The *null-lines* of as many SiN bands as possible were measured on the plates, the setting being made at the point of minimum intensity. In some bands where the head is at a considerable distance from the null-line, the latter appears as a distinct narrow gap in the shading; in others where it is nearer, as a mere lightening; these effects can be seen in the reproductions (Plate I). Settings on the null-lines are subject to rather greater uncertainty than in the case of heads, but it is thought that the data are nearly as accurate as for the latter. One cause of error is the asymmetry in the rate of increase of blackening on the two sides of the null-line. This should tend to displace the settings away from the heads, but study of the question indicates that the error so introduced is unimportant. In the case of bands where the null-lines were not directly measurable, their positions were calculated from those of the corresponding heads, the necessary correction being obtained from a study of the manner in which the distance from head to null-line varies with the vibrational quantum numbers in the directly measurable cases (see next section).

Measurements on the  $\text{Si}^{29}\text{N}$  and  $\text{Si}^{30}\text{N}$  heads, made wherever possible, are given in Table II. Measurements on null-lines were here impossible, since these are concealed by the shading of the much more intense  $\text{Si}^{28}\text{N}$  bands.

#### RESULTS OF MEASUREMENTS ON SiN BANDS

*Analysis of band structure.* The bands consist of two branches, one starting in each direction from the null-line, the positive branch (starting toward higher frequencies) forming a head. The bands are not resolved near the null-line, nor anywhere in the positive branch; but in the negative branch, they become resolved at a moderate distance from the null-line, and can be followed for some distance (cf Plate I). It is reasonable to assume, in accord with their general appearance, that the bands are of the same type as the violet cyanogen bands, with a single missing line (the null-line) in the otherwise continuous series of lines expressible by the equation<sup>12</sup>

$$\nu = \nu^0 + B' \pm 2B'm + Cm^2. \quad (1)$$

In Eq. (1) the positive and negative signs refer to the positive and negative branches, respectively;  $m$ , denoting the rotational quantum

<sup>12</sup> Cf A. Sommerfeld, *Atombau und Spektrallinien*, 4th ed., pp. 718-34.

number of the final state, is assumed to have half-integral values; for the null-line,  $m = -1/2$ ;  $\nu^0$  corresponds to the change of electronic plus vibrational energy.

Measurements were made on the resolved negative branch lines of the (3,2), (4,3), (5,4), and (4,4) bands, which are at the violet end of the spectrum, where resolution is most complete. By plotting first differences of successive lines, the coefficient  $C$  was determined for each of these bands; these values of  $C$  are given in Table I. Substitution of  $m = -1/2$  in Eq. (1) gives for the null-line  $\nu = \nu^0 + \frac{1}{4}C$ , which is equal within experimental error to  $\nu^0$ , the wave-number of the band-origin,<sup>13</sup> since  $\frac{1}{4}C$  is here negligible. For the head,<sup>12</sup>  $\nu = \nu^0 + B' - B'^2/C$ . Letting  $H$  represent the distance from null-line to head, we then have,

$$H = B' - B'^2/C. \quad (2)$$

The  $H$  values are obtainable from the data of Table II, and it is now possible to obtain  $B'$  for each of the four bands; the results are given in Table I.<sup>14</sup>

TABLE I

*Experimental values of  $B'$  and  $C$ .*

[Note: The data in bold-face type were determined from measurements on structure lines; the remaining data were calculated from the  $H$  data of Table II ( $H$  = distance from null-line to head) assuming  $B'$  values calculated from Eq. (3). The data are all in wave-number units.]

$n'$	$n''$	$B'$	$-C$	$n'$	$n''$	$B'$	$-C$	$n'$	$n''$	$-C$
3	2	0.686	0.0303	3	3	0.0245		4	5	0.0255
4	3	0.685	0.0365	4	4	0.0305	0.704	5	6	0.0288
5	4	0.680	0.0403	5	5	0.0336		6	7	0.0323
0	0		0.0117	6	6	0.0384		3	5	0.0152
1	1		0.0161	7	7	0.0441		4	6	0.0198
2	2		0.0199	2	3	0.0161		5	7	0.0244
				3	4	0.0210		6	8	0.0264

Now  $B'$  should be expressible in the form  $B' = (h/8\pi^2 J') - \alpha' n' = B_0' - \alpha' n'$ , and  $C (=B' - B'')$  in the form  $C = C_0 - \alpha' n' + \alpha'' n''$ . From the data on  $C$  for the four measured heads, preliminary values of  $\alpha'$ ,  $\alpha''$ , and  $C_0$  can be obtained. From  $\alpha'$  and the  $B'$  data for the four bands, a preliminary value of  $B_0'$  is then obtained, and from it and  $\alpha'$  can be calculated the  $B'$  value for each value of  $n'$ . From these and the  $H$

<sup>13</sup> Cf R. S. Mulliken, Phys. Rev. 25, 119-138 (1925). For definition of "origin," see p. 123.

<sup>14</sup>  $B'$  could also be obtained by extrapolating the first difference curve (a straight line) in a suitable way to the null-line, but this method is incapable of accuracy. The values of  $B'$  and  $C$  given in Table I were, however, obtained by adjusting the curve in such a way as to give a correct extrapolation to the null-line and at the same time to agree with the measured values of  $H$ .

values obtainable from the data of Table II, a large number of  $C$  values (see Table I), corresponding to a variety of combinations of  $n'$  and  $n''$ , can be calculated; and from these, more accurate values of  $\alpha'$ ,  $\alpha''$ , and  $C_0$  than before can be obtained. By repeating the calculation of  $B_0'$  with the new value of  $\alpha'$ , and so on, by successive approximations (one or two suffice), the following results are obtained:

$$B' = 0.728 - 0.0097 n'; C = -0.0121 - 0.0097 n' + 0.0053 n''. \quad (3)$$

From Eq. (3) the values of  $B'$  and  $C$ , and so of  $H$ , can be calculated for any values of  $n'$  and  $n''$ . Values of  $H$  so obtained were used to reduce the data of Table II, in the cases where heads alone could be measured, to the corresponding values for null-lines. It should be noted that calculated values of  $H$  for this purpose could have been obtained in a purely empirical way from the measured values by studying the way in which the latter vary with  $n'$  and  $n''$ . The results would have been only slightly different, so that the subsequent analysis of the null-line data is practically independent of any possible doubts as to that of the band structure. The procedure actually used amounts to employing the theory as a means of determining the functional relation of  $H$  to  $n'$  and  $n''$ , and then using the measured values of  $H$  to determine the necessary constants so as to calculate unmeasured  $H$  values.

*Dimensions of SiN molecule.* From the above-determined values of  $B_0'$  and  $C_0$ , can be calculated the moment of inertia and interatomic distance of the vibrationless SiN molecule in its initial and final electronic states. From  $B_0'$  one gets  $J_0' = 3.78 \times 10^{-39}$  gm cm<sup>2</sup>, and  $r_0' = 1.567 \times 10^{-8}$  cm. From  $B_0'' (= B_0' - C_0)$  one gets  $J_0'' = 3.72 \times 10^{-39}$  gm cm<sup>2</sup>, and  $r_0'' = 1.554 \times 10^{-8}$  cm. The values of  $r_0$  are considerably greater, as would be expected, than for the CN molecule, where  $r_0$  is  $1.17 \times 10^{-8}$  cm for what is probably the normal state.

Although the writer believes that the foregoing analysis is correct, it would obviously be desirable to study the bands under sufficient dispersion to give complete resolution in the region of the null-lines at least. Also, it may well be that the band lines, which appeared single with the dispersion used, actually consist of narrow doublets as in the violet CN bands.

*Analysis of null-line data.* In order to obtain an equation for the null-lines of the SiN bands, it is convenient to arrange the null-line data of Table II in a rectangular array like Table III, merely substituting them for the intensities of Table III. By an analysis of data

TABLE II  
 Wave-number data on  $S_1N$  bands<sup>1</sup>

Vibr. num. $n'$ $n''$	Si <sup>28</sup> N bands				Isotopic displacements <sup>5</sup>					
	Head	J-M <sup>2</sup>	Null-line <sup>3</sup>	O-C <sup>4</sup>	Si <sup>29</sup> N heads			Si <sup>30</sup> N heads		
					Rotl. <sup>6</sup>	Calc. <sup>6</sup>	Obs. <sup>7</sup>	Rotl. <sup>6</sup>	Calc. <sup>6</sup>	Obs. <sup>7</sup>
6 3	26402		26393	-5						
7 4	26135		26127	-4						
8 5	25863		25856	0						
9 6	25577		25571	-4						
2 0	26213	-1	26196	-3						
3 1	26007		25993	-2						
4 2	25787		25775	-1						
5 3	25554	3	25543	-1						
6 4	25309.7	3	25299.9	0						
7 5	25054.7	3	25045.9	0						
8 6	24790.8	3	24782.9	-1						
9 7	24518		24511	-5						
1 0	25259.1	2	25234.8	2						
2 1	25080.3	2	25060.5	0						
3 2	24886.5	3	24870.3	0						
4 3	24678.4	3	24664.8	1						
5 4	24457.0	2	24444.8	0						
6 5	24223.9	3	24213.0	-1						
7 6	23981.8	3	23972.1	-1						
8 7	23731.4	4	23722.7	-1						
9 8	23473	-7	23465	-3						
10 9	23212		23205	-4						
0 0	24280.6	3	24234.5	0	-0.5	-0.5	....	-1.0	-1.0	.....
1 1	24127.8	2	24095.0	0	-0.4	+0.5	....	-0.7	+1.0	.....
2 2	23960.4	2	23934.5	-1	-0.2	1.7	....	-0.5	3.2	.....
3 3	23778.3	2	23757.7	0	-0.2	3.0	3.1	-0.4	5.7	5.5
4 4	23581.7	2	23564.6	0	-0.2	4.4	4.5	-0.3	8.4	8.8
5 5	23372.9	2	23358.5	0	-0.1	6.0	5.4	-0.2	11.2	11.2
6 6	23152.9	2	23140.6	0	-0.1	7.6	6.9	-0.1	14.3	15.1?
7 7	22924.1	3	22913.6	0	-0.1	9.2	10.0	-0.1	17.3	18.7
8 8	Masked by or fused with 3,4 head									

Si<sup>29</sup>N and Si<sup>30</sup>N heads concealed in this region by shading of Si<sup>28</sup>N heads.

<sup>1</sup> For intensity data, see Table III. For the isotope heads, the intensities are all very low (0 to 000), as can be seen from Plate I.

<sup>2</sup> J-M = excess of Jevons' measured wave-number over the writer's. Blanks in this column represent bands not measured by Jevons.

<sup>3</sup> The values in bold-face type were measured directly. The other values were calculated from the data on the heads with the help of Eqs. (2) and (3): see discussion in paragraph following Eq. (3).

<sup>4</sup> O-C = Observed minus calculated. The calculated values are from Eq. (4).

<sup>5</sup> Isotopic displacement = wave-number of Si<sup>29</sup>N or Si<sup>30</sup>N head minus that of corresponding Si<sup>28</sup>N head.

<sup>6</sup> The calculated isotopic displacement for any head consists of two parts, a small (negative) *rotational* contribution (for method of calculation see second paragraph under "Confirmation of the isotope effect") and a larger *vibrational* contribution (see third paragraph under "Confirmation of isotope effect"). The "calc." (calculated) displacement is the sum of these two contributions, of which only the former is given explicitly in the table.

<sup>7</sup> The deficiency of observed data in the low-frequency part of the spectrum is in all cases attributable to insufficient intensity of the isotope heads, or, when so stated in the table, to masking by structure lines from a preceding head.

TABLE II—continued  
Wave-number data on SiN bands<sup>1</sup>

Vibr. num. <i>n'</i> <i>n''</i>		Si <sup>28</sup> N bands				Isotopic displacements <sup>8</sup>					
		Head	J	M <sup>2</sup>	Null-line <sup>3</sup> O—C <sup>4</sup>	Si <sup>29</sup> N bands		Si <sup>29</sup> N heads			
						Rotl. <sup>6</sup>	Calc. <sup>6</sup>	Obs. <sup>7</sup>	Rotl. <sup>6</sup>	Calc. <sup>6</sup>	Obs. <sup>7</sup>
0	1	Not found									
1	2	Not found (although reported by Jevons)									
2	3	22856.6			22824.6	2					
3	4	22684.5	-4		22660.6	2	Masked by structure lines, etc., but also apparently abnormally weak.				
4	5	22499.8	0		22480.5	1	-0.2	10.3	9.5	-0.4	19.8 19.6
5	6	22302.4	2		22285.7	0	-0.1	11.7	11.2	-0.2	22.4 22.3
6	7	22094.6	2		22080.1	-1	-0.1	13.2	13.4	-0.2	25.1 25.7
7	8	21878.5	-2		21866.3	0	-0.1	14.7	15.5	-0.2	27.8 31.2?
8	9	21656.2	-8		21645.5	1	Masked by structure lines, etc.				
0	2	Not found									
1	3	Not found									
2	4	21772.3			21723.3	-1					
3	5	21605.6	-10		21572.8	0					
4	6	21431.6	-2		21407.0	1	-0.2	16.0	15.2	-0.4	30.9 31.6
5	7	21246.3	-2		21226.8	0	Present but masked by structure lines.				
6	8	21052.0	-5		21035.3	0	-0.1	18.6	19.1?	-0.2	35.7 37.2?
7	9	20848.8	-9		20834.7	1					
8	10	20637.5			20625.4	1					
9	11	20415			20404	-4					
4	7	20381.2			20346.5	0					
5	8	20206.0	2		20180.2	0					
6	9	20021.3			20000.9	-1					
7	10	19830.4			19813.7	0					
8	11	19631			19617	0					
9	12	19421			19409	-5					
6	10	19006			18980	-1					

TABLE III

*Intensity distribution in Si<sup>28</sup>N bands.* The intensities are estimated photographic intensities for a green-sensitive plate, and apply to each band as a whole, not to its head; for data on the heads, reference may be made to Jevons' paper.<sup>2</sup> The  $\Delta n=0$  sequence is indicated by the use of bold-faced type.

<i>n''</i> →	0	1	2	3	4	5	6	7	8	9	10	11	12
<i>n'</i> 0	5	...	...	...	...	...	...	...	...	...	...	...	...
↓ 1	0	4	...	...	...	...	...	...	...	...	...	...	...
2	000	1	6	1	2	...	...	...	...	...	...	...	...
3	...	0-	2-	10	3	3	...	...	...	...	...	...	...
4	...	...	0	2	8	2	2	00	...	...	...	...	...
5	...	...	...	0+	2+	5	3	1+	00	...	...	...	...
6	...	...	...	000	0+	2	2	2	0+	0	0+	...	...
7	...	...	...	...	0-	0	1	1	0	0+	...	...	...
8	...	...	...	...	...	0-	0-	1	?	0	0	0	...
9	...	...	...	...	...	...	00	00	0	...	...	00	00
10	...	...	...	...	...	...	...	...	...	0	...	...	...

on the intervals between adjacent rows and columns, the following equation is then obtained, capable of representing all the null-lines

to within the amounts given in the "Obs.-Calc." column of Table II:

$$\nu = 24234.17 + 1016.30 \, n' - 17.773 \, n'^2 + 0.410 \, n'^3 \\ - 0.00487 n'^4 - 1145.00 n'' + 6.570 n''^2. \quad (4)$$

The comparatively large coefficients of the cubic and biquadratic terms in  $n'$  are unusual, but such terms are definitely needed to represent the data. The relationship between the coefficients of the initial and final states is of a normal type. Since null-lines and origins<sup>13</sup> are probably practically coincident for the SiN bands (cf. discussion preceding Eq. (2)), Eq. (4) should hold equally for both.

#### CONFIRMATION OF THE ISOTOPE EFFECT

For each observed  $\text{Si}^{29}\text{N}$  and  $\text{Si}^{30}\text{N}$  head, comparison is made in Table II of the observed isotopic displacement<sup>13</sup> with that theoretically calculable. For a given band-head, the displacement should be the sum of a small rotational part corresponding to the distance from band-origin to band-head, and a larger vibrational part corresponding to the distance from system-origin to band-origin.<sup>13</sup> The rotational displacement must in every case be negative, since the distance  $H$  (head minus origin, cf. Eq. (2)) is positive in the SiN bands, and is less for the two heavier isotopes than for the lightest isotope  $\text{Si}^{28}\text{N}$  with which the other two are compared. The vibrational displacement should also be negative on the high frequency side of the system-origin, with the result that in each band the  $\text{Si}^{29}\text{N}$  and  $\text{Si}^{30}\text{N}$  heads are superposed on the shading from the  $\text{Si}^{28}\text{N}$  head and so escape detection. On the low-frequency side of the system-origin, however, the vibrational displacement is positive, so that, as soon as the effect of the small negative rotational displacement is overcome, the isotope heads stand out clearly on the high-frequency side of the  $\text{Si}^{28}\text{N}$  head, where there is usually nothing to obscure them seriously. This can be seen in the reproductions (Plate I), where most of the heads of Table I are visible.

The rotational isotopic displacement for a given band can be determined by calculating  $H$  of Eq. (2) for  $\text{Si}^{28}\text{N}$  and subtracting the result from the corresponding value for  $\text{Si}^{29}\text{N}$  or  $\text{Si}^{30}\text{N}$ . For  $\text{Si}^{28}\text{N}$ , the values of  $B'$  and  $C$  used in calculating  $H$  are obtained from Eq. (3); for the other isotopes, the following equations (3') and (3'') must be used:

$$\text{Si}^{29}\text{N} : B' = 0.7196 - 0.00953 \, n'; \\ C = -0.01196 - 0.00953 \, n' + 0.00521 \, n'' \quad (3')$$



$$\text{Si}^{30}\text{N} : B' = 0.7118 - 0.00938 n';$$

$$C = -0.01183 - 0.00938 n' + 0.00512 n'' \quad (3'')$$

The constant terms of (3') and (3'') are obtained<sup>13</sup> by multiplying the corresponding terms of Eq. (3) by  $\rho^2$ , and the coefficients of the  $n'$  and  $n''$  terms by multiplying the coefficients of Eq. (3) by  $\rho^3$ . In general  $\rho^2 = (1/M_2 + 1/M') / (1/M_1 + 1/M')$ . In the present case  $M' = 14$  (the atomic weight of N),  $M_1 = 28$ , and  $M_2$  is either 29 or 30. For  $\text{Si}^{29}\text{N}$ , the values of  $\rho$ ,  $\rho^2$ ,  $\rho^3$ , and  $\rho^4$  are as follows: 0.994236, 0.988505, 0.982808, and 0.977142; for  $\text{Si}^{30}\text{N}$ , they are 0.988826, 0.977777, 0.966852, and 0.956026.

The vibrational isotopic displacement for any band can be obtained in a similar way, using Eq. (4) for the  $\text{Si}^{28}\text{N}$  band, and subtracting the result from that obtained by Eq. (4') or (4'') for  $\text{Si}^{29}\text{N}$  or  $\text{Si}^{30}\text{N}$ . Eqs. (4') and (4'') are obtained from (4) by multiplying each coefficient in the latter by a power of  $\rho$  equal to the power of  $n'$  or  $n''$  with which the coefficient is associated, the constant term being left unchanged since no electronic isotope effect is to be expected.<sup>13</sup>

$$\begin{aligned} \text{Si}^{29}\text{N} : \nu^0 = & 24,234.17 + 1010.44 n' - 17.569 n'^2 + 0.403 n'^3 \\ & - 0.00476 n'^4 - 1138.40 n'' + 6.494 n''^2 \end{aligned} \quad (4')$$

$$\begin{aligned} \text{Si}^{30}\text{N} : \nu^0 = & 24,234.17 + 1004.96 n' - 17.394 n'^2 + 0.396 n'^3 \\ & - 0.00466 n'^4 - 1132.21 n'' + 6.424 n''^2 \end{aligned} \quad (4'')$$

Practically, of course, equations obtained by subtracting (4) from (4') or (4''), respectively, are convenient in the calculation of vibrational isotopic displacements.

Comparison of observed with calculated isotopic displacements in Table II shows complete agreement, within experimental error, throughout the range of  $n'$  and  $n''$  values for which data could be obtained.<sup>15</sup> This thoroughgoing agreement seems the more remarkable when it is noted that each calculated isotopic displacement is the sum of a number of terms involving a variety of powers of  $\rho$ .<sup>16</sup> But such a detailed

<sup>15</sup> The apparent slight increase of the observed displacements relative to the calculated, as  $n'$  is increased, may be real but is within experimental error; note especially that the largest discrepancies are in the cases of the (7,7), (7,8) and (6,8) heads, which were the three weakest heads that were measurable. Also, the calculated displacements may be slightly in error due to inaccuracy in the coefficients of Eq. (4).

<sup>16</sup> The calculated values are considerably larger (especially for larger values of  $n$ , where the higher power terms in  $n$  have their greatest effect) than they would be if calculated according to the approximate relation<sup>13</sup> (which would be exact if there were no higher power terms)  $(\nu_2^n - \nu_1^n) = (\rho - 1)\nu_1^n$ ,  $\nu_1^n$  being the vibrational part of the emitted frequency for  $\text{Si}^{28}\text{N}$  (equal to wave-number for given band-origin minus that for system-origin). For example, the correct calculated vibrational displacement for the (7,7) band of  $\text{Si}^{30}\text{N}$  is 17.40, whereas the value obtained by the above approximate relation is  $(22914 - 24235)(-0.011174) = +14.76$ .

agreement, if any at all, is to be expected, since the theory is of such a nature that its detailed predictions in regard to the various coefficients all stand or fall together.<sup>17</sup>

The agreement of the observed with the calculated isotope effect is evidence against the possibility that half-integral quantum numbers ( $\frac{1}{2}$ ,  $1\frac{1}{2}$ ,  $2\frac{1}{2}$  . . . .) should have been employed instead of the integral numbers (0, 1, 2, . . . .) actually used in the calculation. If half-integral numbers were applicable, all the calculated values of Table II should be increased to approximately the mean of the given value and the value for the band having values of  $n'$  and  $n''$  both one unit greater; this increase amounts to about 0.8 units for  $\text{Si}^{29}\text{N}$  and 1.4 units for  $\text{Si}^{30}\text{N}$ . As a matter of fact, however, there are distinct indications<sup>15</sup> that there may be an effect of this sort masked by a small constant displacement in the other direction. The mean value of the observed minus calculated isotope effect is  $-0.1$  for  $\text{Si}^{29}\text{N}$  and  $+0.4$  for  $\text{Si}^{30}\text{N}$  (giving half weight to observed data marked doubtful, and omitting the value 31.2 for the 7,8 band). Adding 0.9 to all observed values would bring these averages to 0.8 and 1.3, respectively, which are very near the amounts 0.8 and 1.4 above calculated. Such a relative displacement in the measured, as compared with the true, interval between a  $\text{Si}^{29}\text{N}$  or  $\text{Si}^{30}\text{N}$  head and a corresponding  $\text{Si}^{28}\text{N}$  head is not inconceivable, in view of the enormous difference of intensity. Hence the question of half vibrational quantum numbers for  $\text{SiN}$  cannot be considered definitely settled in the negative. It should be further noted that the existence of integral quantum numbers here would be in contradiction to the probable close analogy of  $\text{SiN}$  to  $\text{BO}$  for which the evidence<sup>9</sup> is strongly in favor of the half-integral numbers.

The evidence of the isotope effect in favor of  $\text{SiN}$  as emitter of the present bands is more definite. The only compounds other than  $\text{SiN}$  whose theoretical isotopic displacements are at all near those observed are  $\text{SiC}$  and  $\text{SiO}$ . The former need not be considered; for the latter, the value of  $(\rho-1)$  is  $-0.00629$  for  $\text{Si}^{29}\text{O}$  and  $-0.01220$  for  $\text{Si}^{30}\text{O}$ . These are about 9 percent greater than the corresponding values for  $\text{SiN}$ ; and the same is true for  $(\rho^2-1)$ ,  $(\rho^3-1)$ , etc., since, approximately,

<sup>17</sup> Although, of course, the observed agreement does not constitute a quantitative confirmation of theory for the small higher power terms, it does involve a close agreement for the linear and at least approximate agreement for the quadratic terms. An attempt to obtain equations for the  $\text{Si}^{29}\text{N}$  and  $\text{Si}^{30}\text{N}$  heads directly from the experimental data (such a method was used in the case of  $\text{B}^{10}\text{O}$  and  $\text{B}^{11}\text{O}$ ) in order to compare the coefficients with those of Eq. (4) for  $\text{Si}^{28}\text{N}$ , would not have been of much value here, on account of the fewness of the data on the isotope heads.

$(\rho^2 - 1) = 2(\rho - 1)$ ,  $(\rho^3 - 1) = 3(\rho - 1)$ , etc. Hence, every term in (and so the total magnitude of) any calculated isotopic displacement, must be about 9 percent greater for SiO than for SiN. If one adds 9 percent to each of the calculated displacements of Table II, it is apparent that the agreement with the observed displacements becomes much poorer than at present.<sup>18</sup> This evidence in favor of SiN is strongly supported by the chemical evidence previously cited. The fact that the known SiO bands<sup>10</sup> are not obtained with the present bands and have no coefficients in common with those of the latter also supports the case against SiO as a possible emitter of the present bands.

#### INTENSITY DISTRIBUTION IN THE SiN BANDS

*Rotational distribution.* The reproductions show strikingly, especially for the bands belonging to the sequence for which  $\Delta n = 0$ , the rise in intensity in each branch from the null-line. In the negative branch, the intensity can be seen to rise rather rapidly to a maximum and then to fall slowly; in fact, irradiation at the end of the image of the slit on the plate has traced for each band a sort of flattened intensity distribution curve resembling that for a Maxwellian distribution. A similar rise to a maximum in the positive branch, followed by a fall before the head is reached, can be seen in the (0,0) and less clearly in the (1,1) band. Of course the apparent intensity distribution is greatly affected, especially in the positive branch, where also there is the overlap of lines returning from the head, by the changing spacing of the lines. A very rough estimate of the position of the most intense line in each branch, after attempting to discount the above effects, gives  $m_{max} = 13$ . For thermal equilibrium, this would correspond by the equation  $T = (1.431)(2B)m_{max}^2$  to a temperature of 80°C, a reasonable figure for the actual temperature, and similar to the result obtained by Birge in the case of the CN bands generated in active nitrogen.<sup>3</sup>

*Vibrational distribution.* As in the cases of BO and CN, the low effective temperature indicated by the rotational quantum number distribution is belied by the vibrational energy distribution. Instead of the very rapid fall of intensity from intense bands with  $n' = 0$  to very weak bands with  $n' = 1$  and undetectable intensity for higher  $n'$  values, the summed emission intensity actually rises from  $n' = 0$  until  $n' = 3$ , and then falls gradually (cf Fig. 1). This type of phenomenon

<sup>18</sup> It should be noted that the effect of substituting half-quantum numbers, and that of substituting SiO for SiN, both would produce an increase of the calculated isotopic displacements, so that there is no possibility of a mutual cancellation of the two effects.

has been discussed in previous papers<sup>19,20</sup> on BO and on CuI, to which reference should be made.

The intensity distribution with respect to observed values of  $\Delta n$  appears to be very similar to that in the violet CN bands,<sup>21</sup> and of a type indicating, according to Lenz's theory, that the motion of the excited electron is unusually little affected by the vibration of the molecule. The sequence  $\Delta n=0$  is by far the most intense,  $\pm 1$  are fairly strong, while  $+2$ ,  $-2$ ,  $+3$ ,  $-3$ , and  $+4$  (the last represented only by one weak head, which may be spurious) follow in diminishing order of intensity. In spite of the restricted range of  $\Delta n$  values as compared with cases such as BO and CuI, two relations found to hold for the latter<sup>19,20</sup> are also clearly present in the SiN bands. These are a preference for positive over negative  $\Delta n$  values, and a tendency, also noted in several additional cases by Birge,<sup>20</sup> for the numerically larger  $\Delta n$  values to be associated with the larger values of  $n'$ . The general preponderance of intensity in Table III on the positive side of the diagonal drawn through the members of the sequence  $\Delta n=0$ , shows the existence of the first relation. The second is shown by the increasing length of the *rows* of figures in Table III as  $n'$  increases; particular attention may be called to the low intensity of the bands (1,0), (2,0), and (0,1), (1,2), (0,2), (1,3), the last four not having been found at all.<sup>22</sup> An explanation of these effects in terms of Lenz's theory has been given in the paper on CuI.<sup>20</sup>

#### NEW SYSTEM OF BANDS IN THE SILICON NITRIDE SPECTRUM

In addition to the intense system of SiN bands discussed above, which for convenience will in the following be called the A bands of SiN, a number of additional, but very much weaker bands, are

<sup>19</sup> See ref. 9, p. 292-3, (BO).

<sup>20</sup> See ref. 8, pp. 20-24, (CuI); also abstract of paper by R. T. Birge, *Phys. Rev.* **25**, 240 (1925), in regard to  $n'$  and  $\Delta n$  distribution.

<sup>21</sup> The resemblance is well brought out when the CN bands are obtained by the action of active nitrogen on carbon compounds. In the violet CN bands, the dominance of the sequence  $\Delta n=0$  and the tendency toward the restriction of  $\Delta n$  to small values are much as in the SiN bands, but perhaps somewhat less marked. Although the violet CN bands are shaded toward the violet, not toward the red like the SiN bands, this difference is a superficial one from the theoretical standpoint, being due to the fact that the coefficient  $C$  has small positive values in the first case and small negative values in the second case.

<sup>22</sup> This is partly due to the weakness of the *heads* of these bands, due to their large (calculated) distance from the null-lines in this region. But if the bands had been at all intense, the region of maximum intensity on either side of the null-line would certainly have been seen.

TABLE IV

*Wave-number data on heads of new bands.*

Heads marked "masked" are concealed usually by bands of the more intense SiN system. Heads marked \* appear only as emphasized structure lines of a SiN or NO band; in the case of those marked †, two heads fall together; those marked ? are of doubtful identity as members of the system.

Wave-numbers for  $n'=7$ ,  $n''=0$  should be added to the Table. They are 31372 and 31348.

$n' \rightarrow$	0	1	2	3	4	5	6	
$n'' \downarrow$	0	.....	.....	28050*678	28728 673	29401 664	30065 657	30722 650
		.....	.....	28017*682	28699 674	29373 665	30038 659	30697 651
			1019	1018	1021	1022	1020	1020
			1012	1017	1019	1020	1027	1027
1	.....	26348†683	27031 679	27710 670	28380 663	29043 659	29702*	29702*
	.....	26318 687	27005 677	27682 672	28354 664	29018 652	29670*	29670*
		1005	1008	1009	1009	1008		
			1004	1010	1010	1014		
2	.....	25343 680	26023 678	26701 670	27371 664	28035*		
	.....	Masked	26001*671	26672 672	27344 660	28004*		
		1001	997		998			
					996			
3	.....	24342 684	25026	Absent	26373	.....	.....	.....
	.....	24318	Absent	Absent	26348*	.....	.....	.....
					979			
					978			
4	Masked	.....	.....	Absent?	25394	.....	.....	.....
	22649	.....	.....	Absent	25370	.....	.....	.....
	970							
5	21708 691	22397 689	23086	Masked	.....	.....	.....	.....
	21679 691	22370 688	23058 681	23739?	.....	.....	.....	.....
		958						
		957						
6	.....	21439	Absent or	22802 668	23470*	.....	.....	.....
	.....	21412	Masked	Masked	23438*			
		943		937	943			
		943						
7	19804 692	20496 685	21181 684	21865?662	22527	Absent or	.....	.....
	19784 685	20469 685	21154 679	21833?	Masked	Masked		
	931	934	933	938				
	935	930	936	938				
8	18873†689	19562 686	20248 679	20927	Absent or	.....	.....	.....
	18849†690	19539 679	20218 677	20895	Masked	.....	.....	.....
		923	921					
		931	915	913				
9	.....	18639?688	19327		20678	.....	.....	.....
	.....	18608*695	19303 679	19982 674	20656	.....	.....	.....
			911		910			
			912	910				
10	.....	.....	18416 681	19097 671	19768	.....	.....	.....
	.....	.....	18931*681	19072	.....	.....	.....	.....
				894	895			
				895				
11	.....	.....	.....	18203 670	18873†	.....	.....	.....
	.....	.....	.....	18177 672	18849†	.....	.....	.....
					877			
					880			
12	.....	.....	.....	.....	17996	.....	.....	.....
	.....	.....	.....	.....	17969	.....	.....	.....
					[866]			
					[864]			
13	.....	.....	.....	.....	.....	[663]17793	.....	.....
	.....	.....	.....	.....	.....	[663]17768	.....	.....

present. Their presence is obvious only in the near ultraviolet and in the green, but on careful examination it was found that they extend through the intervening region and belong to a single system. They are all shaded toward the red, and in the ultraviolet, where conditions are most favorable, are seen to become resolved, at a moderate distance from the head, into a series of structure lines. The heads are in pairs of about equal intensity, with a separation averaging 26.8 wave-number units and apparently constant or nearly so.

Measurements, of no great accuracy, were made on the heads of the new bands in the hope of finding possible relations between them and the A bands. The wave-number data are given in Table IV, and the intensities in Table V. The former are so arranged as to show the

TABLE V

*Intensity distribution in new bands (estimated photographic intensities). Vacant spaces represent bands not found; a few of these may be weakly present but masked by heads of the more intense SiN system.*

$n'' \rightarrow$	0	1	2	3	4	5	6	7	8	9	10	11	12	13
$n' \downarrow$														
0	...	...	...	...	00	0	...	0-	0+	...	...	...	...	...
1	...	0-	0	0-	...	1	0+	1	0-	0+?	...	...	...	...
2	00	1-	1-	(2)	...	0	...	0+	1	2+	0	...	...	...
3	0-	1	1	...	...	0?	0+	0?	0	0	1+	1	...	...
4	1-	2-	0	0-	0	...	1-	0	...	1	00	0+	1	...
5	0	0	00	...	...	...	...	...	...	...	...	...	...	0
6	0-	000	...	...	...	...	...	...	...	...	...	...	...	...
7	00	...	...	...	...	...	...	...	...	...	...	...	...	...

constant differences between adjacent rows and columns which is the basis of the assignment of vibrational quantum numbers made. On account of the peculiar intensity distribution, the absolute numbering is somewhat uncertain in respect to  $n'$ , but is quite definite in regard to  $n''$ , since there is no indication of additional bands in the ultraviolet beyond the relatively intense series for which  $n'' = 0$ . The positions of the heads of the new bands can be represented approximately (a systematic analysis to determine the best values of the coefficients has not been made) by the equation:

$$\nu = \left\{ \begin{matrix} 26676 \\ 26649 \end{matrix} \right\} + 694n' - 3.3n'^2 - 1025.9n'' + 6.4n''^2. \quad (5)$$

From a comparison of Eqs. (4) and (5) it is evident that the new bands have no term in common with the A bands. Although the new bands are presumably due to SiN, there is no definite proof of this from the isotope effect; but this could not have been expected, on account of the low intensity of the bands even in the most intense exposures.

Observations on the new bands showed them to be quenched in the same manner as the A bands by small amounts of oxygen. This indicates that they are due to the same emitter. Also, the numerical values of the coefficients and the spacing of the structure lines are of the same order of magnitude as for the A bands. It is possible, of course, that the new bands are not due to SiN, but to some other diatomic emitter such as Si<sub>2</sub> or SiP. SiCl must be ruled out, since the relative abundance of the isotopes of chlorine is such that both SiCl<sup>35</sup> and SiCl<sup>37</sup> heads should have been visible even with the low intensities used.<sup>23</sup>

TABLE VI  
*Unidentified heads or lines in SiN spectrum.*

Wave-No.	Type	Int.	Wave-No.	Type	Int.	Wave-No.	Type	Int.
24267		1	22777	v	3-	21088		1d
149	l?	0	745	v	3-	071		1d
23989	l?	3	446	v?	0	20816	l?	0
960		0	423	v?	0+	773	r	0-d
871	1	0+	016	v	1+	736	r	0-d
836	1	1+	21970	l?	*0+	146	v?	00
712		0	963	l?	*0+	142	v?	00
232	l?	1+	925	v?	1-	19993	r	00
176	l?	1	914	v?	0+			
22997	l?	3	822	v?	1			
985	l?	3-	818		0			
970	v?	2+	800	v?	1			
949	v?	1	797		0			
894	v	3	715	l?	1-			
870	v	3	291	v?				

Notes: l = line; v = shaded toward violet; r = shaded toward red; d = diffuse;  
\* means superposed on structure line.

The intensity distribution (cf Table V) in the new bands is of an interesting type characterized by a preference for numerically large  $\Delta n$  values, and by the non-occurrence of the band (0→0) and neighboring bands. This distribution approaches that typified by the visible iodine bands.<sup>24</sup> It indicates that the motion of the emitting electron is very markedly affected by the vibration of the molecule.—It should be stated that Tables IV and V include all bands of appreciable intensity, except possibly at the extreme red end.

From the analogy of SiN to CN one might expect in the red or near infrared a system of SiN bands analogous to the red CN bands. No such bands were found, presumably because they lie too far in the infrared. Possibly the new SiN system has for its final electronic state a doublet state identical with the initial state of the hypothetical red SiN bands. In

<sup>23</sup> Also, these bands have not been reported by Jevons (Proc. Roy. Soc. 106A, 174, 1924) in his investigation of the discharge through pure SiCl<sub>4</sub> vapor.

<sup>24</sup> Cf refs. 12 and Birge, ref. 20; and especially R. Mecke, Phys. Zeits. 26, 234 (1925).



addition to the new bands and the A bands, there are a number of unidentified lines or heads; the data are given in Table VI. Some of these are rather intense, and many are shaded toward the violet; it is possible that these last will prove of importance in the spectrum of SiN.

The writer wishes to express his gratitude to Prof. G. P. Baxter of the Chemistry Department for the pure  $\text{SiCl}_4$  used in the above work.

JEFFERSON PHYSICAL LABORATORY,  
HARVARD UNIVERSITY,  
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## THE IONIZATION OF HCl BY ELECTRON IMPACTS

By E. F. BARKER AND O. S. DUFFENDACK

## ABSTRACT

**Ionization of HCl.**—Current-voltage curves obtained by means of a two electrode, hot cathode discharge tube indicate ionization in stagnant HCl gas at 14 volts in agreement with the value of the ionizing potential reported by previous observers. Spectrograms showed no hydrogen lines at voltages near the ionizing potential, but they appeared faintly at higher voltages along with some bands. A considerable amount of dissociation of the gas was observed, and this was shown to be due to thermal action at the filament rather than to the discharge. The presence of dissociation products made the interpretation of the critical potential doubtful, and so the apparatus was modified to eliminate these from the region of observation. With HCl flowing continuously through a three element discharge tube in such a way that it passed through the observation chamber, where the electron impacts occurred, before it reached the filament, no hydrogen lines appeared at accelerating voltages up to 120 volts. Current-voltage curves again show a *critical potential* at 14 volts which is attributed to the ionization of the molecule without dissociation. No *band spectra* of wave-lengths between 6000 and 2000Å accompany this excitation. Hence it is concluded that the molecule has no electron transitions involving a change of energy between 2 and 6 volts. When an  $\text{HCl}^+$  ion is neutralized, the electron is probably bound in a single operation with the consequent radiation of energy equivalent to about 14 volts.

**Effect of HCl on a tungsten filament.**—The conductivity was observed to increase 10 percent in 5 hr. Langmuir suggests that  $\text{WCl}_6$  formed at the cooler ends is dissociated at the hot section.

THE ionization potential of HCl has been measured by Foote and Mohler,<sup>1</sup> by Knipping,<sup>2</sup> and by Mackay.<sup>3</sup> These observers agree on the numerical value of the ionizing potential, but disagree in their interpretation of the process of ionization. Foote and Mohler report 14 volts and suggest that it corresponds to the dissociation of the HCl molecule into a positive hydrogen ion and a negative chlorine ion. This interpretation is based upon the fact that the work involved in the production of these ions from the molecule, which can be computed from known heats of reaction, is equivalent to 13.7 volts. Mackay reports 13.8 volts for the ionizing potential but finds no evidence of dissociation and concludes that the process involves simply the removal of one electron from the molecule. He used a modified Lenard method of

<sup>1</sup> Foote and Mohler, Amer. Chem. Soc. Jour. **42**, 1832 (1920).

<sup>2</sup> Knipping, Zeits. f. Phys. **7**, 328 (1921).

<sup>3</sup> Mackay, Phil. Mag. **46**, 828 (1923) and Phys. Rev. **23**, 553 (1924).

measurement<sup>4</sup> employing a photo-electric source of electrons and thus eliminating thermal dissociation of the molecule. We find that the latter point of view is confirmed by a spectroscopic study of the impact region when HCl is subjected to an intense electronic bombardment.

#### METHOD

In the early experiments of this investigation, HCl was generated by dropping concentrated  $\text{H}_2\text{SO}_4$  on pure  $\text{NH}_4\text{Cl}$ , dried by passing over  $\text{P}_2\text{O}_5$  and admitted at pressures of 0.01 to 0.2 mm into a simple two electrode discharge tube. The cathode was a 12 mil (0.3 mm) tungsten spiral, and the anode a platinum plate. The minimum voltages at which an arc could be struck and maintained were determined under varying conditions of pressure and filament temperature. As ionization is essential for the striking and maintaining of an arc, this minimum voltage is the ionizing potential of the gas unless ionization by cumulative action occurs, and it apparently did not occur in our experiments. The results obtained are in agreement with the value of the ionizing potential reported by the previous observers. Spectrograms were taken of these arcs in HCl with glass and quartz spectrographs, and these were examined especially for the Balmer lines of hydrogen which should appear if  $\text{H}^+$  ions are found in any appreciable concentration in the region of the arc or if hydrogen gas is present in appreciable amount.

The appearance of  $\text{H}\beta$  on the plates and the gradual accumulation of a gas not condensable at the temperature of liquid air indicated that some dissociation of the HCl had occurred. This was found to be due largely to thermal action at the filament, however. It was consequently necessary to so modify the procedure as to eliminate as far as possible the effects of these decomposition products from our observations. This was accomplished by employing an apparatus arranged as shown in Fig. 1, in which diffusion of gases from the neighborhood of the filament into the region of observation is minimized. A molybdenum diaphragm, fitting the tube closely, was inserted between the filament and the plate—about 1 mm from the former and connected to the plate by a wire. This divided the tube into two compartments and separated the filament from the region of electron impacts. A fine platinum gauze covered a small aperture in the diaphragm and served as a window for the passage of the gas through the tube and of electrons from the filament. A continuous flow of HCl through the observation chamber and towards the cathode was maintained, the rate being controlled by a

<sup>4</sup> Compton and Mohler, Critical Potentials, Nat. Research Coun. Bull. 48.

special stopcock *S*, with an indicator and scale. The gas passed out of the discharge tube through an arm sealed on directly above the filament and was condensed in the second liquid air trap shown in the diagram. The pump was operated continuously during a run to take off any uncondensed gas. A field for accelerating electrons was set up between the filament and the gauze, and the electrons passing through the gauze made impacts with the HCl molecules in an equipotential region between the diaphragm and plate. The radiation from this region was photographed with a small Hilger quartz spectrograph through a quartz

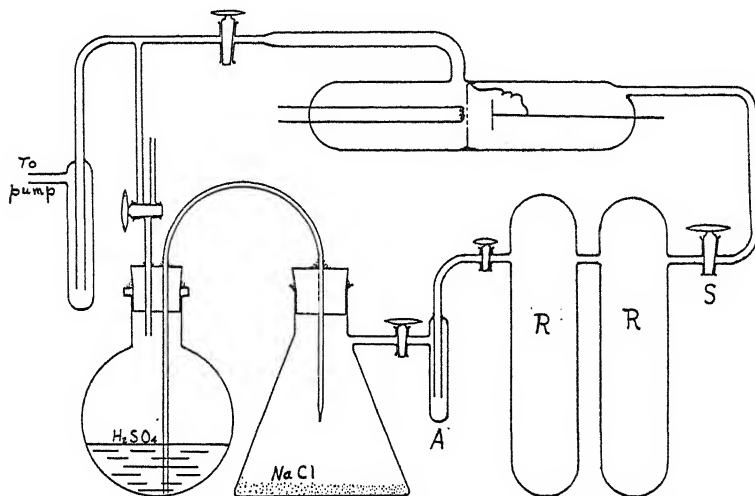


Fig. 1. Arrangement of apparatus for providing a continuous flow of HCl through the discharge tube.

window sealed on to the discharge tube, and the combined grid and plate current was measured for various accelerating voltages and gas pressures. The results indicate that the effects of dissociation at the filament and of chemical action following such dissociation were completely eliminated.

An adequate supply of HCl was prepared in advance. Concentrated  $\text{H}_2\text{SO}_4$  and  $\text{NaCl}$  of the highest purity were introduced into the generator shown in Fig. 1 and the whole system evacuated. Then air was admitted above the  $\text{H}_2\text{SO}_4$  in the flask causing the acid to drop slowly upon the salt. The evolved gas was collected up to atmospheric pressure in the reservoir *R*, the stopcocks closed, and the excess HCl allowed to escape through the acid flask. Liquid air was next applied to the trap *A*, condensing the HCl and any water vapor which might have

been present. The reservoir was then opened to the pump once more, and a small amount of uncondensed gas which was present was pumped off. Finally, about two-thirds of the condensed HCl was permitted to evaporate into the reservoir, the remainder being released through the generator. The gas thus collected was found to contain no detectable impurities.

### RESULTS

Typical current-voltage curves for the *stagnant* gas are shown in Fig. 2, in which the arc current is plotted against the accelerating volt-

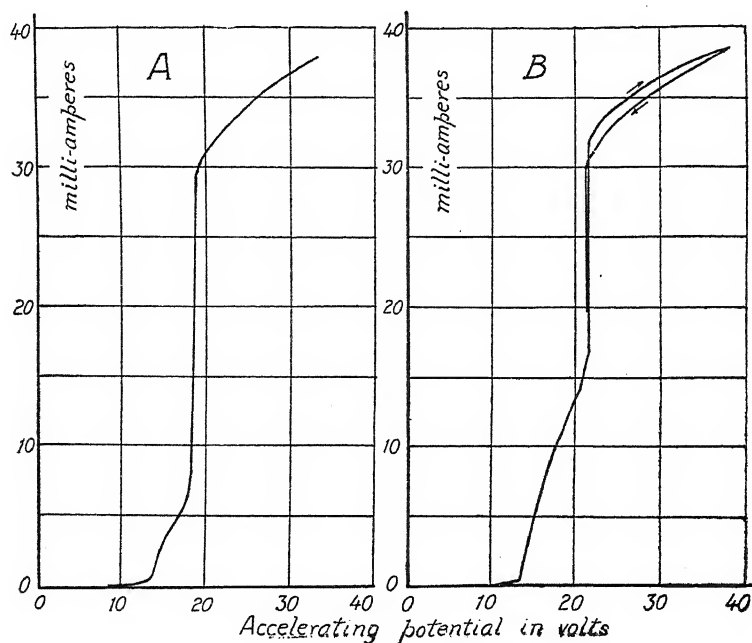


Fig. 2. Current-voltage curves in stagnant gas. The arc current in milli-amp. is plotted against the accelerating voltages. Initial pressure 0.15 mm for curve A and 0.06 mm for curve B.

age. In each an abrupt increase in current at about 14 volts is apparent, while the arc struck at somewhat higher potentials, the values of which are a function of the pressure of the gas and the temperature of the filament. The arcing potential seemed also to depend somewhat upon how long the gas had been in the tube.

The discharge was entirely colorless. At voltages above 37 the spectroscope showed  $H\beta$  faintly. Exposures of several hours at accelerating potentials up to 60 volts showed only the hydrogen lines and some

bands in the ultraviolet. These bands did not appear consistently on the plates and were probably due to accumulated reaction products, perhaps chlorine and metallic chlorides. While the tube was operating there was a noticeable clean-up of the gas, and after each run it was found that a considerable fraction of the residual gas would not condense in a liquid air trap. This must have been hydrogen, and the appearance of the Balmer lines is thus accounted for. The interpretation of the critical potential at 14 volts is in doubt, however, so long as other gases are present in the discharge tube.

Typical ionization curves obtained *with gas flowing* through the tube are shown in Figs. 3 and 4. In Fig. 3, curve *a* was obtained with no gas in the tube, and curve *b* directly afterward with a continuous flow of HCl. The arc struck at about 20 volts, but ionization set in at 14

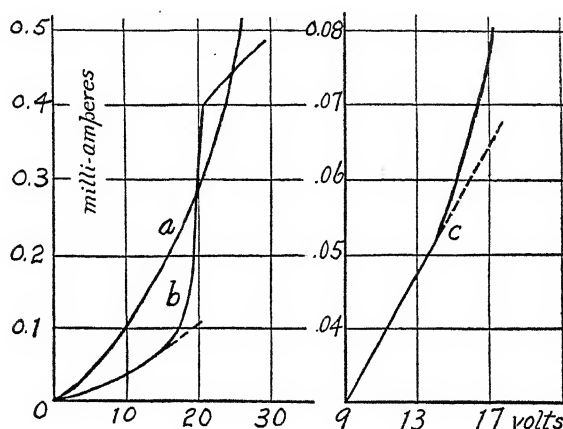


Fig. 3. Current-voltage curves. The arc current in milli-amp. is plotted against the accelerating voltages. Curve (a) without gas; (b) with HCl flowing; (c) part of curve b magnified.

volts. This is apparent from the change in curvature along a small part of this curve when plotted to a larger scale as shown in curve C. The abrupt change in slope between 13 and 14 volts is at once evident. The curve of Fig. 4 represents conditions similar to those of Fig. 3(b), and shows no other discontinuities up to 120 volts. Runs like these were made for pressures up to 0.1 mm with various filament temperatures. The average of the ionization potentials indicated is about 14 volts.

The spectrograph failed to reveal any radiation whatsoever between 6000 and 2000Å when pure HCl gas flowed continuously through the apparatus. Even the Balmer lines were missing, though exposures

were made with accelerating potentials as high as 120 volts. This fact, together with the absence of deposits on the plate side of the molybdenum diaphragm resulting from reactions of the gas after contact with the filament, led to the conclusion that the gauze and gas stream were effective in keeping the observation region free from impurities.

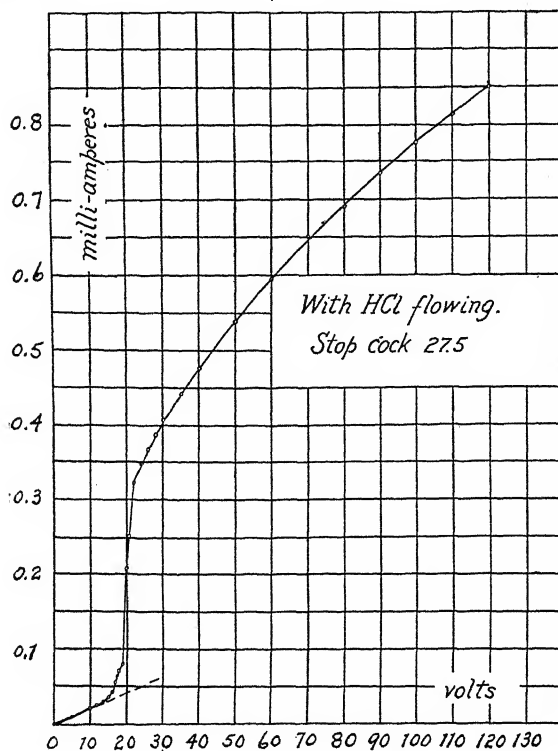


Fig. 4. Current-voltage curve for flowing gas, 0-120 volts.

The effect of the gas upon the filament is of particular interest. In Fig. 3, curves *a* and *b* were obtained with the same filament current. It will be noted that the thermionic emission for voltages below the arcing potential is very much less when gas is flowing. This is partly due to the cooling of the filament by the gas, and partly, perhaps, to a modification of the emitting surface by chemical action. The behavior of the filament in the presence of the gas was unusual in that its conductivity, instead of decreasing with use, increased throughout nearly the whole of its life. As computed from the ratio of the currents required to produce a certain potential drop across the filament, the conductivity in one instance increased over ten percent in five hours with



gas flowing at a pressure of about 0.1 mm.<sup>5</sup> Accompanying this action there is dissociation of the HCl, for a McLeod gauge near the mercury diffusion pump always read zero when the filament was cold and read about 0.0003 mm when the filament was hot. As the liquid air completely removed the HCl, this pressure was due to some dissociation product, undoubtedly hydrogen. The approximate rate of thermal dissociation was determined by shutting off the pump and heating the filament in stagnant gas. After 45 minutes it was found that about one-third of the gas remaining in the tube failed to condense in the liquid air trap. No increase in the amount of accumulated hydrogen was observed under similar conditions when an arc of 1.5 milli-amp. was maintained in the tube. This indicates that the amount of dissociation by electron impacts is entirely negligible compared with that produced by thermal action, and the failure of the hydrogen lines to appear supports this conclusion. The absence of dissociation in the arc implies that at the critical potential of 14 volts a molecular ion of HCl is formed.

The fact that no radiation of wave-lengths between 6000 and 2000Å appears indicates that the molecule has no electron transitions involving a change of energy between 2 and 6 volts. After recapturing an electron, therefore, the normal state must be reached by a single transition, or else by combinations of steps of less than 2 and more than 6 volts. The behavior of other molecules indicates that two nearly equal steps are hardly to be expected. Also the fact that no critical potentials have been detected below that of ionization indicates the binding of the electron in a single operation with the consequent radiation of energy equivalent to about 14 volts.

PHYSICS LABORATORY,  
UNIVERSITY OF MICHIGAN.  
June 9, 1925.

<sup>5</sup> We are indebted to Dr. Langmuir of the General Electric Company for an explanation of this effect. The cooler parts of the filament are attacked by atomic chlorine from the dissociated HCl,  $\text{WCl}_6$  being formed. This compound has a considerable vapor pressure at the temperature of the tube. The vapor is decomposed at the hot section of the filament, and metallic tungsten deposited there. The central part of the filament assumed a granular appearance after being heated in the gas due to this crystalline layer. Cf Langmuir, *Amer. Chem. Soc. Jour.* **37**, 1162 (1915).

CRITICAL POTENTIALS IN SECONDARY ELECTRON  
EMISSION FROM IRON, NICKEL, AND  
MOLYBDENUM

BY ROBERT L. PETRY

## ABSTRACT

Secondary electron emission from iron, nickel and molybdenum targets for primary voltages 0 to 1500.—The tube used was designed so as to minimize disturbing factors, all metal parts were glowd before assembly, and the tube was baked before each set of runs. In addition the targets were thoroughly cleaned by heating to bright red by electronic bombardment from an auxiliary filament until a permanent condition was obtained as indicated by the curves. The pressure was kept below  $10^{-6}$  mm. Both the secondary emission  $I_1$  and the primary current  $I_2$  were measured by a null method of high precision (to 0.1 percent or less). The ratio  $I_1/I_2$  was found (1) to vary only 2 percent as the retarding potential between the plate and surrounding box was increased from 3 to 10 volts, so 6 volts was considered sufficient; (2) to vary only slightly with the primary current; (3) to be unchanged when the earth's magnetic field was neutralized. The final curves, for all three metals after heat treatment, are nearly alike, the value of  $I_1/I_2$  rising to a maximum of about 1.30 at about 348 volts for iron, 455 volts for nickel and 356 volts for molybdenum. From slight breaks (changes of slope) in the curves, some 25 critical potentials were located for iron, 16 for nickel and 20 for molybdenum. The values below 40 volts for iron (7.3, 11.6, 14.4, 18.3, 22.6, 25.0 and 29.0) and for nickel (6.2, 9.3, 9.9, 11.8, 15.1, 22.6, 24.4, 31.4, 35.0) agree fairly well with critical potentials for soft x-rays determined by Thomas. This suggests that there is a common phenomenon involved in the production of secondary emission and of soft x-rays which is evident at the lower voltages but which is masked at higher voltages by other processes not yet understood.

## INTRODUCTION

IT HAS been known for some time that when electrons strike a metal surface in a vacuum they cause the emission of secondary electrons from the metal. The work of the earlier investigators<sup>1-10</sup> in this field

<sup>1</sup> A. Gehrts, *Ann. der Phys.* **36**, 995 (1911).

<sup>2</sup> N. Campbell, *Phil. Mag.* **22**, 276 (1911); **25**, 803 (1913); **28**, 286 (1914); and **29**, 369 (1915).

<sup>3</sup> A. W. Hull, *Phys. Rev.* **7**, 1 and 141 (1916).

<sup>4</sup> H. M. Dadourian, *Phys. Rev.* **14**, 434 (1919).

<sup>5</sup> J. T. Tate, *Phys. Rev.* **17**, 394 (1921).

<sup>6</sup> Davisson and Kunsman, *Science* **54**, 394 (1921).

<sup>7</sup> I. G. Barber, *Phys. Rev.* **17**, 332 and 292 (1921).

<sup>8</sup> L. E. McAllister, *Phys. Rev.* **21**, 122 (1923).

<sup>9</sup> Horton and Davies, *Proc. Roy. Soc.* **97A**, 23 (1920); *Phil. Mag.* **46**, 129 (1923).

<sup>10</sup> E. W. B. Gill, *Phil. Mag.* **45**, 864 (1923).

has shown that (1) the number of secondary electrons emitted depends on the nature of the metal and is a function of the velocity with which the primary electrons strike, (2) the number of secondary electrons, at the higher voltages, may exceed the number of primary electrons striking, so that reflection alone is not sufficient to account for the phenomenon, and (3) the emission is dependent upon the previous heat treatment of the metal bombarded. Recently Farnsworth<sup>11</sup> has made a careful study of the ratio of secondary emission to primary current for various metals after careful heat treatment and has investigated the effect of heat treatment of copper upon its emission. Stuhlman<sup>12</sup> observed, in the case of iron, that the relation between the number of secondary electrons per primary electron and the velocity of the primary electrons changes more or less abruptly at certain values of velocity, thus indicating critical velocities (or voltages) for secondary emission.

The object of the present investigation has been to determine more exactly whether the number of secondary electrons emitted per primary electron changes gradually as the velocity of the primaries is increased, or whether at certain critical velocities this number changes abruptly. It was assumed that a considerable part of the secondary emission, if not all of it, might be due to the photo-electric action of soft x-radiation which is caused by the electronic bombardment of the metal surface and which acts photo-electrically on the metal itself in which it originates; if this is the case, a relation or correspondence should be found between these critical velocities for secondary emission and those for x-ray emission.

#### APPARATUS AND PROCEDURE

The apparatus used was of the same form as that used by Campbell<sup>2</sup> and A. W. Hull.<sup>3</sup> Electrons from a filament  $F_1$  (Fig. 1) were drawn toward a series of diaphragms with openings SSS by a field  $V_1$ , and all those passing through the openings struck a metal plate  $P$ . Any electrons reflected from  $P$  or emitted as secondary electrons were drawn by a field  $V_2$  to a nickel cylinder  $CC$  almost completely surrounding  $P$ . The current to  $CC$  was measured by a galvanometer  $G_1$ , and the total current through SSS by a second galvanometer  $G_2$ .

The plate  $P$  was mounted through a ground glass joint sealed on the outside with DeKhotinsky cement, so that it could be replaced or

<sup>11</sup> H. E. Farnsworth, Phys. Rev. 20, 358 (1922) and 25, 41 (1925); Proc. Nat. Acad. Sci. 8, 251 (1922).

<sup>12</sup> Stuhlman, Science, 56, 344 (1922); Phys. Rev. 25, 234 (1925).

taken out for polishing without cutting the tube. The ground glass joint was long and was kept free from cement except at the outside, where it was kept cool by water circulation; consequently the cement vapor pressure was small because of the difficulty of diffusion between the ground glass surfaces and because of rapid evacuation by the pumping system. The filament  $F_1$  was mounted similarly through another ground glass joint.

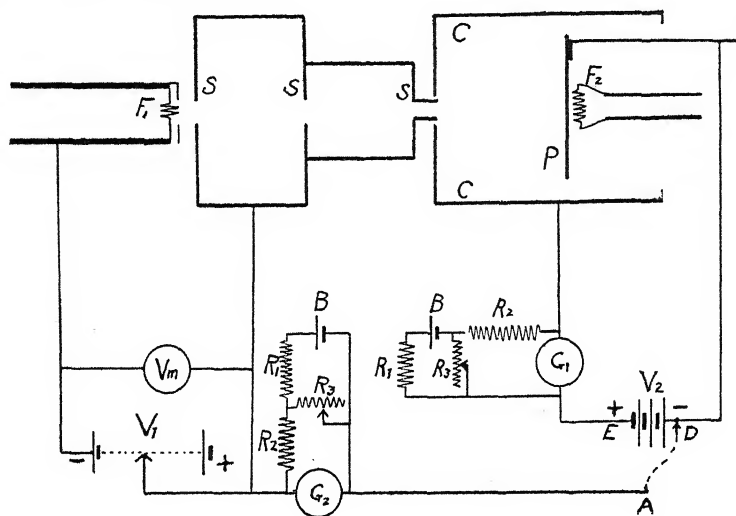


Fig. 1. Diagram of apparatus and electrical connections.

The filament  $F_1$  was of 10 mil (.25 mm) tungsten wire helically wound in three closely-spaced turns of small diameter so as to give a small, nearly equipotential source of electrons. The heating current required varied from 5.8 to 6.3 amp., with a potential drop of 1.1 to 1.2 volts. This current was supplied by a large capacity insulated storage battery, which was used under conditions suitable for giving the greatest possible constancy of the current. A rheostat consisting of a nichrome ribbon immersed in kerosene, with heavy clamp contacts, was found to furnish a very steady control resistance. A focusing ring of nickel sheet was mounted a short distance in front of the filament but the potential applied to it was found to have little effect upon the amount of current passing through the openings, and in most of the runs it was left connected to the negative filament terminal.

The system of three diaphragms  $SSS$  and the cylinder  $CC$  were of nickel and both were mounted directly against the walls of the glass tube which was of 3.5 cm diameter. These two parts were so designed

as to give about an inch of glass insulation between them. The diaphragms were spaced 1.5 cm apart and the openings were circular holds 2.5 mm in diameter. The distance from the filament  $F_1$  to the plate  $P$  was 5 cm.

All metal parts were glowd out in an induction furnace before being assembled, in order to remove occluded gases. Before each set of runs all parts of the tube, with the exception of the water cooled DeKhotinsky seals and two charcoal traps in series with it, were baked out for several hours in electric furnaces at a temperature of about 400°C. Liquid air was kept on a third trap continuously in order to keep mercury and oil vapors from entering the tube. A second filament  $F_2$  was mounted directly back of the plate  $P$ , and after the tube was allowed to cool the plate was glowd out several times at a bright red heat by electronic bombardment from  $F_2$  in order to remove occluded gases from the surface to be bombarded. The temperature used in this process was sufficient to cause the iron target to show signs of melting at the point nearest the filament. As a result of these precautions, with the diffusion pump running continuously and liquid air on both charcoal traps, during runs the pressure was too small to be detected by a McLeod gauge reading to  $(10)^{-6}$  mm of mercury.

The accelerating potential  $V_1$  was varied from 0 to 1500 volts. Storage cells were used up to 300 volts, while for higher ranges a motor-generator set run by storage batteries was used.  $V_1$  was adjusted by a 12,000 ohm potentiometer system and was measured by a Weston Laboratory Standard Voltmeter with a scale of 750 divisions and with suitable multiplying resistances to give convenient ranges.

The retarding potential  $V_2$  was usually about 6 volts and was furnished by dry cells. Part of the runs were taken with the connections shown but most of the later ones were taken with  $A$  (Fig. 1) connected to  $E$  instead of to  $D$ , so that the strong field in the close gap between the projecting tube of  $SSS$  and the edge of the hole in the end of  $CC$  was avoided. The accelerating field from  $F_1$  to  $P$  was then  $V_1 - V_2$ . The results from the two methods of connecting were indistinguishable.

It will be noted that the current reflected directly back through the opening in the end of  $CC$  was lost. This could cause the observed ratio of secondary electrons to primary electrons to be smaller than the actual ratio. However, the solid angle subtended at  $P$  by the opening was not more than 2.5 percent of the entire solid angle and the loss was assumed to be negligible. In any case this source of error should not affect the location of critical potentials.

Multiple reflection and emission from *CC* back to *P* have also been neglected. However, velocity distribution measurements by Farnsworth and the writer indicate that a collecting potential  $V_2$  of 6 volts should be sufficient to avoid any considerable final reflection or emission from *CC* to *P* since a large proportion of the secondary electrons have velocities insufficient to carry them against this collecting field.

The current to *CC* was usually of the order of  $(10)^{-6}$  amp. and was measured by a galvanometer  $G_1$  of sensitivity better than  $(10)^{-9}$  amp. per scale division. In order to measure the total current coming through *SSS* and striking *P* the second galvanometer  $G_2$  was connected so as to measure the current to both *P* and *CC*; that is, the electrons remaining on *P* plus those reflected or emitted from it to *CC*. The filament current was adjusted so that, except at the lowest voltages, this current through  $G_2$  was greater than  $(10)^{-6}$  amp., while the sensitivity of  $G_2$  was about 5  $(10)^{-9}$  amp. per scale division.

In order to obtain greater precision the galvanometers were not shunted in measuring the larger currents, but were used at full sensitivity for all ranges by a method of balancing currents, in which the galvanometer measured only the residual current after approximate balancing by the following potentiometer method. Whenever the scale reading of one of the galvanometers became large it was reduced to near zero by sending an additional current through the galvanometer in the reverse direction by means of a storage cell *B* connected through two high resistances  $R_1$  and  $R_2$  and a shunt  $R_3$  of low variable resistance. In this way the major part of the current to be measured was balanced by an accurately known reverse current, while the galvanometer, at full sensitivity, measured the difference between these two. As the currents increased, during a run, it was necessary to change this balancing current at intervals; the correction factor to be added at each step-down of this kind in the scale reading was not computed but was observed directly for each change of  $R_3$  by noting the difference between readings taken before and after changing  $R_3$ , all other factors remaining constant. A reliable check on the steadiness of conditions during this change for one galvanometer was given by observations on the readings of the other galvanometer. Below 50 volts the currents were generally satisfactorily steady but above that range there were generally slow and regular drifts of both currents in the same ratio; under these conditions duplicate readings were taken on changing  $R_3$  in order to determine the correction satisfactorily. The largest current

measured in this way was the equivalent of about 4000 scale divisions of the galvanometer used.

The ratio of the current through  $G_1$  to the current through  $G_2$  gives the number of secondary electrons emitted from the target per electron striking it. This ratio  $I_1/I_2$  was plotted as ordinate against  $V_1$  (or  $V_1 - V_2$  with changed connections) in volts as abscissa. The resulting curves showed breaks or places of rapid change of slope. In order to locate these accurately, readings were taken at small voltage intervals. In the region 0 to 24 volts the intervals were 0.2 volts; in the region 650 to 1500 volts, 10-volt intervals were used, while intermediate intervals were used in the intermediate regions. The correction in the value of  $V_1$  for initial velocity of the electrons was estimated at 0.2 volts and for potential drop to the middle of the filament was 0.55 volts; but the correction for contact difference of potential is not known accurately. Hence, the total correction due to these causes was checked experimentally for iron and nickel by observing the retarding potential  $-V_2$  with  $A$  connected to  $E$ , which was necessary to keep the majority of electrons from reaching  $P$  under an accelerating field  $V_1$ . This correction was  $-0.4$  volts for iron and  $+0.8$  volts for nickel.

The present investigation differs from other studies made in the same field in the smaller voltage intervals used in taking readings and in the precautions taken to measure the currents and the accelerating voltage precisely while avoiding disturbing factors.

## RESULTS

Preliminary observations were made to determine the effect upon the ratio of secondary emission to primary current of four factors, viz., variation of collecting potential  $V_2$ , variation of filament current, compensation of the earth's magnetic field, and heat treatment of the target.

An increase of  $V_2$  from 3 to 10 volts increased the ratio  $I_1/I_2$  by about 2 percent in most cases. Increasing  $V_2$  from 6 to 20 volts had a smaller effect. In general so long as  $V_2$  was not negative it had little effect upon the ratio  $I_1/I_2$  and none at all upon the position of breaks in the graph of  $I_1/I_2$  plotted against  $V_1$ .

Results taken with different filament currents were as consistent as regards critical potentials as were runs taken with the same filament current, hence various filament currents were used throughout and the results were plotted without regard to this factor. In general, however, with an increase of filament current the ratio  $I_1/I_2$  showed a tendency



to decrease slightly; this shows that not the absolute values of the ratio but its relative values for any one run were determined precisely.

A few runs were taken with two long bar magnets placed so as to compensate the earth's magnetic field approximately over the path of the primary electrons. No difference could be distinguished between the results of these runs and the results of runs taken without the magnets. The nickel parts of the apparatus may have provided considerable magnetic shielding for the electron paths.

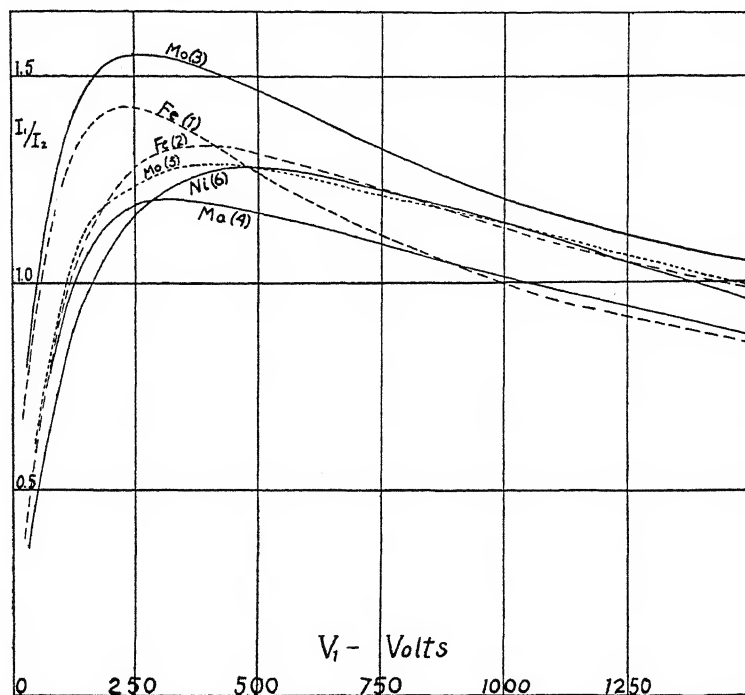


Fig. 2. Number of secondary electrons emitted per primary electron, 0-1500 volts.  
 Curves 1 and 2, Fe before and after heat treatment.  
 Curves 3 and 4, Mo before and after partial heat treatment.  
 Curve 5, Mo in final state.  
 Curve 6, Ni after heat treatment.

The effect of previous heat treatment of the target was not investigated at length. In general this reduced the ratio  $I_1/I_2$  and the curves approached a limiting form in agreement with results found by Farnsworth. A maximum in the ratio was found at about 225 volts for iron and at about 275 volts for molybdenum before glowing out the target by electronic bombardment (curves 1 and 3, Fig. 2); similar maxima

in the same general region, 200 to 275 volts, were reported by Gehrts<sup>1</sup> for copper, aluminium and cobalt targets not glowed out in vacuo. But it was found that after thorough heat treatment this maximum came permanently at 356 volts for molybdenum and at 348 volts for iron (curves 2 and 3, Fig. 4).

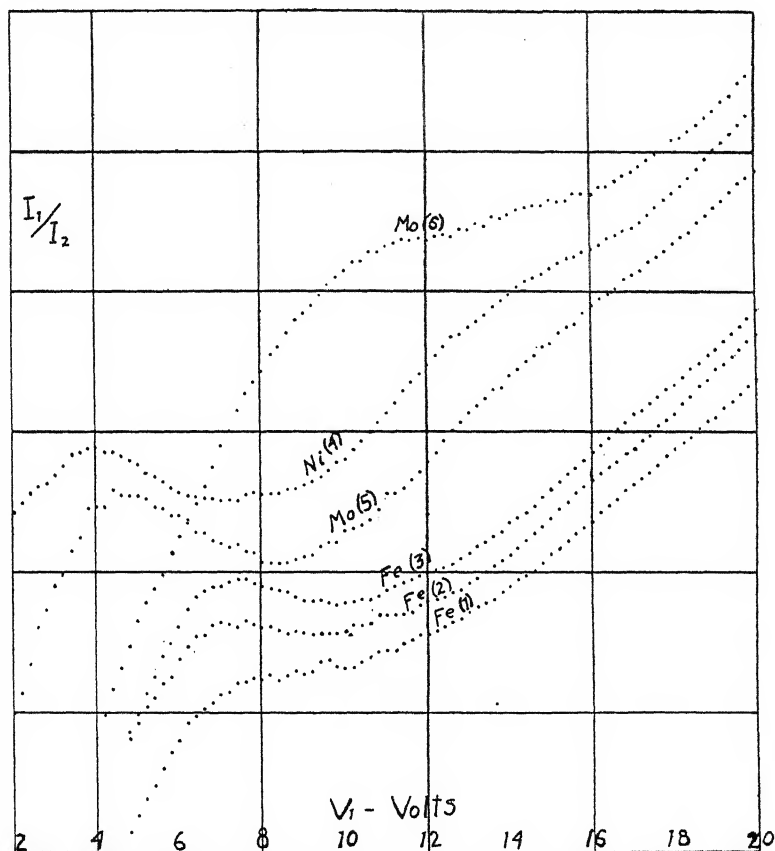


Fig. 3. Secondary emission curves, 2-20 volts. Different scales of  $I_1/I_2$  are used.

Curves 1, 2, and 3, Fe, after thorough heat treatment.

Curve 4, Ni after thorough heat treatment.

Curves 5 and 6, Mo after thorough and after only partial heat treatment.

Heating to a dull red heat failed to bring the molybdenum target to a final state; curves taken at this stage are different in form at low voltages from those taken after the target had been glowed out at a bright red heat (curves 5 and 6, Fig. 3). Also a maximum value of the ratio was reached at 315 volts in this stage instead of at the final value

of 356 volts (curves 1 and 2, Fig. 4). After the target was heated to a bright red heat a few times further heating produced no changes in the shape of the curves.

Breaks are found in the curves for both iron and molybdenum taken before the final state was reached. (No curves of this kind were taken for nickel.) These breaks, however, are not found at the same voltages

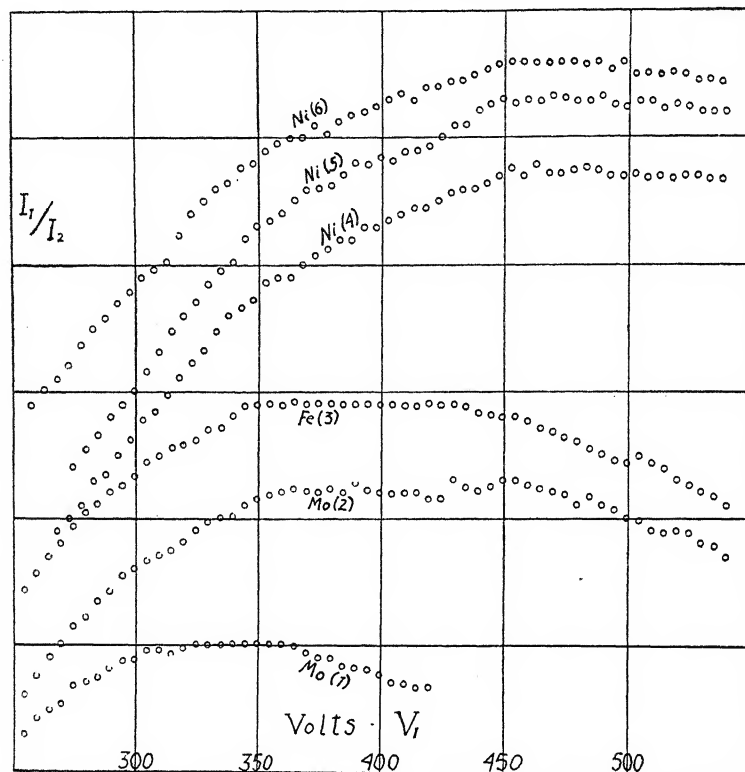


Fig. 4. Curves in region of maxima, 250-550 volts. Different scales of  $I_1/I_2$  are used.  
Curves 1 and 2, Mo after partial and thorough heat treatment.  
Curve 3, Fe after thorough heat treatment.  
Curves 4, 5 and 6, Ni after thorough heat treatment.

as are those for the heat-treated targets and are in general less definite, with more gradual curvature. Even after the final state was reached the ratio at any given voltage might vary a few percent from one set of runs to the next, but the position of breaks was not affected by the change of ratio.

Curves 1 and 2, Fig. 2, show the general variation of  $I_1/I_2$  with velocity of impact up to 1500 volts, for iron before and after glowing

out the target. Curves 3, 4 and 5 show results for molybdenum untreated, after being heated to dull red heat, and in its final state; curve 6 is for nickel thoroughly heat-treated.

Fig. 3 shows the region 2 to 20 volts. Curves 1, 2 and 3 show results for iron taken at different times, all after heat treatment. In the region 7 to 10 volts the slope of the curve was sometimes positive and sometimes negative, but was always set off from the regions adjoining it by

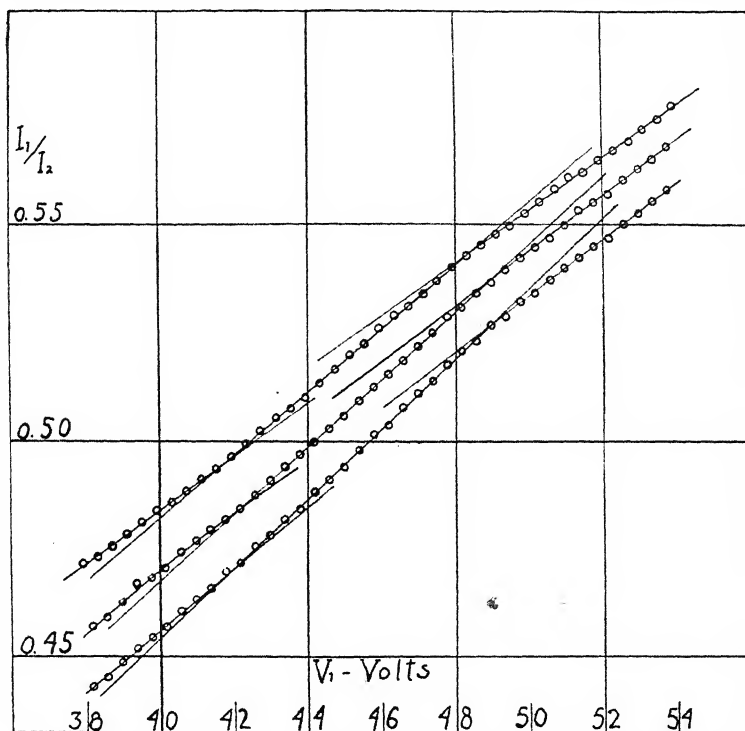


Fig. 5. Secondary emission curves for Fe, 36-56 volts.

changes of slope. Curve 4 is for nickel and curve 5 for molybdenum after careful heating. Curve 6 shows the results for molybdenum after heating to a dull red heat; there seems to be no connection with curve 5. In order to avoid confusion in plotting, these curves are not all plotted to the same scale of  $I_1/I_2$ .

Fig. 4 shows the region of the maximum, with  $I_1/I_2$  plotted on different scales for different curves. Curve 1 is for molybdenum after partial treatment; the maximum value of  $I_1/I_2$  is 1.205 secondary electrons per primary electron. The other curves are all for targets in

the final state and are as follows: curve 2, molybdenum, with maximum value of  $I_1/I_2$  equal to 1.284; curve 3, iron, maximum value of 1.323; curves 4, 5 and 6, nickel, with maximum values of 1.282, 1.280 and 1.253 respectively.

TABLE I  
*Critical primary potentials for iron*

Critical potential (volts)	Weight factor	Sign	General breaks	Soft x-ray levels (Thomas)	Critical potential (Stuhlman)
.....				.....	3.3
7.3	10	+	+7.3	7.3	8.5
11.6	10	-	-11.6	11.1	10.4
14.4	8	+	+14.4	14.1	
	4		+16.2	16.5	
18.3	4	+		19.4	
22.6	4	+		.....	
25.0	2	-		24.3	24.3
29.0	1	+	+30.6	28.8	
.....				34.3, 37.5	
43.6	2	+		41.2	
46.5	4	+		48.	
.....				51.3	50
55.5	2	-		54.6	
63.8	3	-		62.	
.....				67.6	
70.4	3	-	-70.6	.....	
.....				75.3, 82.7	80
85.1	1	+	85.1	87.1	
.....				91.2	
97.6	4	-		94.8	
.....				103.5, 112.2	
119.4	1	-		.....	120
.....				125.7	
157.2	2	-		seventeen	160
175.6	2	-		potentials	171
193.3	(?)	-		omitted	200
227.3	(?)	-			
257	2	-			
290.	1	-	290	288.6	
.....				303.7, 331	
348	5	-	348	.....	
390	1	-		.....	
455	2	-		.....	
.....				639	
720	1	-		704.3	
.....				818.5	
1040	?	+		.....	
1370	?	+		.....	

An indication of the agreement of the results for iron in the region 38 to 54 volts is given by Fig. 5. This region is more satisfactory than the average, however. In particular the region 100 to 400 volts is difficult to interpret; what appears to be gradual curvature in this region may be due to a number of small breaks. Above 500 volts in

iron changes of slope seem to occur at a few fairly definite points in good agreement on all curves; but corresponding points for nickel and molybdenum are hard to locate.

In Table I the first column gives the critical potential for secondary emission from iron determined in the present investigation. In accordance with the suggestions followed by Thomas,<sup>13</sup> the value of the work function for iron, 5 volts, has been added to the observed values. The

TABLE II  
*Critical primary potentials for nickel*

Critical potential	Weight factor	Sign	General breaks	x-rays levels (Thomas)
6.2	2	+		.....
9.3	3	-		8.6
9.9	3	-	-9.9	.....
11.8	5	+		11.74
15.1	3	+	+15.1	14.6
.....				16.56, 18.0
22.6	4	+	+23.5	22.2
.....				.....
24.4	2	+		27.25
.....				30.97
31.4	5	+	31.4	34.6
35.0	2	+		39.8, 44.65
.....				.....
48.2	3	+	+47.	51.3, 54.8
.....				57.4
58.5	1	+		65.6
.....				71.9
72.6	?	-	71.9	79.8
.....				87.2
84.5	1	+		91.2, 94.9
.....				.....
.....			98.3	.....
.....			106.5	.....
115.3	?	-	-115.	116.6
172	?			(fourteen omitted)
262	2		262	265.9
.....				280, 286.5, 294.9
.....				311.5, 341.3
356	5	-	365	.....
455	5	-	455	.....
503	1	-		.....
.....				774, 833.4
.....				948, 1017.3

second column gives an estimate of the importance of the break based on intensity and on definiteness of location. All breaks except those of weight (1) were shown with fair agreement by all curves over the ranges concerned. The third column shows whether the break was due to an

<sup>13</sup> C. H. Thomas, Phys. Rev. 25, 322 (1925).

increase of slope (+) or a decrease (-). The fourth column gives breaks which appear when curves with much larger voltage intervals are plotted, so as to average out all breaks which do not result in a change of slope which persists over at least a considerable voltage interval. The fifth column gives results by Thomas for soft x-ray levels for iron. Breaks observed by Thomas since the paper to which reference is made was published are included. Seventeen breaks between 130 volts and 280 volts have been omitted in this column since comparison between the few values in the first column and the large number found here by Thomas would be without significance. The sixth column gives results for critical potentials in secondary emission from iron reported by Stuhlman.<sup>12</sup>

TABLE III  
*Critical primary potentials for molybdenum*

Critical potential	Weight	Sign	General breaks
4.9	2	+	
7.3	1	-	
8.4	8	-	-8.5
12.7	5	+	+12.7
15.0	2	+	
16.5	1	+	
22.5	3	+	
30.5	4	+	
37.4	2	+	
41.9	3	-	-42
50.7	?	-	
53.9	1	-	
59.3	1	-	
65.8	0	+	
79.5	3	-	-79.
82.8	1	-	
101.9	?	-	
111.4	?	-	
131.3	0	-	
206.5	1	+	
298	2	-	-298
356	4	-	-356
473	1	-	

Table II similarly gives the results of the present investigation with nickel and the unpublished results obtained by Thomas for soft x-ray levels for nickel. Again 5 volts for the work function of nickel have been added to the results of both observers to give the data of columns 1 and 4. Table III shows the breaks observed in secondary emission from molybdenum; 4.3 volts have been added for the work function of molybdenum. No detailed data are available for comparison.



## DISCUSSION OF RESULTS

Tables I and II show good agreement between columns 1 and 5 up to 40 volts. Above that voltage column 5 begins to have more values than column 1 and above 100 volts a comparison would be of no value. The curvature observed in this region in the secondary emission curves may be due to a large number of breaks, each too faint to be located separately. If several breaks of column 5 are interpreted as a single break in column 1 the agreement should disappear. However, no breaks are found by Thomas between 331 and 639 volts for iron and between 341 and 774 volts for nickel, while one of the more definite points in the secondary emission curves, the point at which the ratio reaches a maximum, comes in these regions, at 348 volts for iron and at 455 volts for nickel. Therefore it appears that, in the two investigations different effects have been studied at high voltages and that in the present work the effect of photo-electric emission due to x-radiation is not detectable because of larger effects which mask it.

It has been shown by Farnsworth<sup>11</sup> that a negative break may be accounted for by assuming that inelastic impacts begin to occur at critical voltages so that, after such a collision, neither the primary electron nor the electron with which the collision occurs has sufficient energy to escape from the metal. It may be noted that if the work function of nickel and iron is 5 volts, all electrons with a velocity less than 5 volts will fail to escape from the metal so that the curves might be expected to show negative breaks at the critical potentials for inelastic impact, followed by weaker positive breaks at an interval of 5 volts.

The meaning of the decreasing value for the ratio with increasing velocity of impact at high velocities is in doubt; there is no apparent reason why the probability of escape after a collision should decrease with increasing velocity unless a large part of the primary electrons penetrate to a comparatively great depth before making a collision, so that secondary electrons are less likely to escape.

In conclusion the writer wishes to thank Professor K. T. Compton, at whose suggestion this problem was taken up, for his constant interest and frequent assistance in the work.

PALMER PHYSICAL LABORATORY,  
Princeton, New Jersey.  
May 20, 1925.

NEGATIVE ION EMISSION FROM OXIDE  
COATED FILAMENTS

BY HENRY A. BARTON

## ABSTRACT

Using a tube described by Smyth,<sup>1</sup> it was discovered that oxide-coated, platinum filaments emit negative ions as well as electrons. These ions were shown to be due not to gas in the tube or to gas absorbed by the filament, but to disintegration of the oxide coating itself. Electro-magnetic analysis of these ions, described in this paper, gave the value of  $m/e$  as about 33 with reference to hydrogen ions and indicated that they consisted only of negative, singly charged, molecular oxygen ions. No evidence of the emission of any positive ions was obtained. This negative ion emission apparently begins at a lower temperature than electronic emission, and increases with temperature, but less rapidly than the electronic. The contribution of the negative ions to the space charge is appreciable because of their relatively large mass, causing the space charge limited current for a given voltage to be less than for a similar non-coated platinum filament. Certain observations by other experimenters are discussed and shown to be in support of the above conclusions.

DURING a study of the ions formed by electron impact in argon,<sup>2</sup> the writer observed negative ions in large numbers. These were first thought to be formed by argon atoms but subsequently it was discovered that they were produced even when no argon was present in the experimental tube. A more careful examination of their behavior indicated that they came from the filament and were of smaller mass than argon atoms. The filament then in use was a strip of platinum coated with barium and strontium oxides. After substituting a thoriated tungsten filament the negative ions were no longer observed.

More recently a direct study of this phenomenon has been made. The experimental tube was the one described recently by Smyth<sup>1</sup> modified only by the removal of the gauze electrode next to the filament. The result was a simple arrangement for the accurate electro-magnetic analysis of the particles from a hot source. A new platinum strip was mounted as a filament and a careful search made for negative ion emission. None was observed. The strip was then taken out and given an oxide coating by the following process: Two sticks of paraffin one containing  $\text{BaCO}_3$  and the other  $\text{SrCO}_3$  were touched to the strip

<sup>1</sup> Smyth, Phys. Rev. 25, 452 (1925).

<sup>2</sup> Barton, Phys. Rev. 25, 469 (1925).

alternately while it was maintained at a temperature just too low to give visible radiation. After each application time was allowed for the paraffin to burn off. When a good coating was obtained, the strip and leads were heated red hot in a flame to remove the last traces of hydrocarbons. They were then immediately installed and the tube evacuated. In the subsequent work the pressure in the tube was of the order of  $10^{-4}$  mm.

With the filament at red heat, negative ions of the same mass as before were again observed in large numbers, thus proving that the source of these ions was the oxide coating. The range of  $m/e$  values from about 5 to 95 times the value for the hydrogen nucleus was ex-

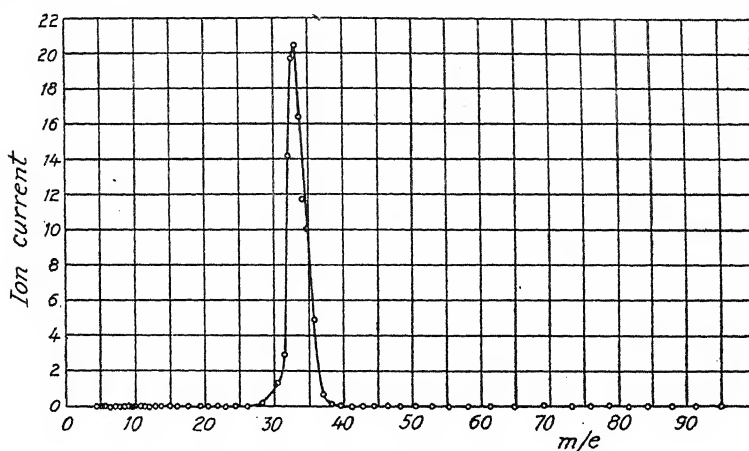


Fig. 1. Mass spectrum of negative ions.

amined and only one group of negative ions was detected. A typical mass spectrum is given in Fig. 1. The fields were then reversed and an attempt made to detect positive ion emission. The  $m/e$  ranges examined included those corresponding to barium and strontium atoms, each with single or double charge, and also the hydrogen range. No positive ions whatever were observed. This checks a previous result with the first coated filament.

*Identity of the ions.* The negative ions observed had an apparent  $m/e$  value of 33. The  $m/e$  scale had been calibrated by known positive ions and may have been slightly inaccurate for negative ions because of lack of perfect reversibility of the electromagnet used. However,  $C_2^-$ ,  $(CO)^-$  and  $A^-$  ions were certainly not present. The paraffin sticks were tested for chlorides and none found to be present. The conclusion, therefore, is that the ions are oxygen molecules, i.e.  $O_2^-$ .

*Other results.* The apparatus was not adapted to a careful study of thermionic emission and no further results were obtained except some determinations of the variation of ion current with the temperature. These merely indicated inconclusively that the ions were first emitted at a temperature too low for electron emission and increased in number as the temperature was raised well into the range in which the electron current was large.

The evidence does not clearly indicate whether the  $O_2$  molecules came off the filament already charged or picked up an electron after emission. The fact mentioned in the previous paragraph favors the former process.

The objection may be raised that not enough time was allowed for the absorbed gases in the oxide coating to be evolved. This objection might be valid in the case of the second filament but not in the case of the first, which had stood continuously in a high vacuum (except for argon at low pressures) for several months and had been burned two or three hundred hours at least.

#### DISCUSSION

The above conclusions receive indirect support from the earlier experiments of several observers. For example, Wehnelt and Jentsch<sup>3</sup> observed that at a given temperature the current from a Wehnelt cathode never quite reached a saturation value as the applied voltage was raised. This is different from the behavior of a pure metal filament in a high vacuum but analogous to its behavior in the presence of a small amount of gas. In other respects oxide filaments have similar properties to pure metal filaments so it is quite likely this difference is due to the oxygen gas which is produced. The nature of the action is not clear.

Fredenhagen<sup>4</sup> observed (1) that the oxide disappears much more rapidly if the filament is heated with a properly directed field applied than with no field, (2) gas is given off when the cathode is in action, and (3) the metal under surface shows corrosion as if an alloy had been formed with the residual barium and strontium metals. The first of these suggests strongly the formation of  $O_2^-$  ions. This is also supported by Horton's<sup>5</sup> conclusion that the conductivity of hot oxides is partly electrolytic. The third observation is in line with the recent suggestion

<sup>3</sup> Wehnelt and Jentsch, *Verh. d. D. Phys. Gesell.* **10**, 605 (1908).

<sup>4</sup> Fredenhagen, *Phys. Zeits.* **15**, 21 (1914).

<sup>5</sup> Horton, *Phil. Mag.* **11**, 505 (1906).

of Koller<sup>6</sup> that the emissive property of the Wehnelt type of filament is due to the deposit of a surface film of the metal reduced from the oxide.

The nearest approach to the writer's work has been done by Schmidt<sup>7</sup> and his collaborators. They found that no positive ions were given off by heated oxides of cadmium and zinc although many salts of these metals do yield positive ions. It appears to be characteristic of oxides that the metal atoms are not emitted, at least not as ions. In regard to the emission of negative particles by these oxides, Schmidt merely mentions their action as Wehnelt cathodes emitting electrons. The construction of his tube apparently did not permit distinguishing between electrons and negative ions.

The effect of the negative ions in contributing to the space charge is very simple. Where the current as limited by space charge consists of two parts,  $i$  due to electrons (mass  $m$ ), and  $I$  due to negative ions (mass  $M$ ), Langmuir's equation for cylindrical electrodes may be re-written

$$i\sqrt{m} + I\sqrt{M} = (2\sqrt{2}/9)\sqrt{e} V^{3/2}/r\beta^2$$

where  $e$  is the electronic charge,  $V$  the applied voltage,  $r$  the radius of the receiving electrode and  $\beta$  a geometrical constant. Since  $I$  is small compared with  $i$ , the latter is practically the observed total current. Therefore the total current is given approximately by

$$i = \frac{2\sqrt{2}}{9} \sqrt{\frac{e}{m}} \frac{V^{3/2}}{r\beta^2} - I \sqrt{\frac{M}{m}}.$$

Although  $I$  is small,  $\sqrt{M/m}$  is quite large so that to obtain the same space charge limited current from an oxide coated filament as from a plain filament, it is necessary to apply a higher voltage. Katsch<sup>8</sup> has recently compared filaments of several types in identical geometrical situations. As would be expected from the above consideration, he finds it necessary to apply a larger potential to get the same current in the case of oxide coated filaments than in the case of tungsten or thoriated tungsten filaments.

The writer wishes to thank Professor K. T. Compton and Dr. H. D. Smyth for their encouragement and helpful suggestions.

PALMER PHYSICAL LABORATORY,  
PRINCETON, NEW JERSEY,  
June 2, 1925.

<sup>6</sup> Koller, *Phys. Rev.* **25**, 671 (1925).

<sup>7</sup> Schmidt, *Ann. der Phys.* **75**, 337 (1924); contains summary of earlier papers.

<sup>8</sup> Katsch, *Zeits. f. Techn. Phys.* **5**, 11, 505 (1924).

THE PERSISTENCE OF THE RADIATION EXCITED  
IN MERCURY VAPOR

BY LUCY J. HAYNER

## ABSTRACT

A photographic method was used. Light from an intermittent mercury arc passed through a quartz cell containing Hg vapor at 40° to 100°C, and then together with the excited radiation through a hole in a rotating sector into a spectrograph. The sector was mounted on the shaft of the commutator which operated the arc. Thus for  $\lambda 2537$  a trace was obtained on the plate, whose length depended on the time of persistence of the radiation, the time scale being determined by the speed of rotation. Measurements of the blackening showed that the decay was exponential. The time to decrease to intensity  $1/e$  came out  $4.0 \times 10^{-8}$  and  $6.8 \times 10^{-8}$  sec. for cells of length 1.6 and 3.2 cm respectively. For the arc alone in a tube of 0.9 cm radius the constant was  $0.6 \times 10^{-8}$  sec, while for the arc at the center of a bulb of 3 cm radius the constant was  $5.5 \times 10^{-8}$  sec. The decay was found to be independent of the vapor pressure from .006 to .27 mm for the cell and from .05 to 1.7 mm for the bulb. No persistence was observed when the cell did not contain distilling mercury or when it was sealed off from the pump. Fresh mercury seems to be necessary and also the absence of impurity. It is interesting to note that the time constants are of the order of magnitude of the times required for atoms at the temperatures involved to go without impact from the center to the wall of the cell.

IN A RECENT series of experiments Webb<sup>1</sup> studied by an electrical method the life of the resonance radiation  $\lambda 2537$  in mercury vapor. The radiation was excited by electron impacts under voltage sufficient to lift the valence electron to the  $2p_2$  orbit. His results gave pressure and dimension relations not in agreement with those required by the "imprisonment theory" of repeated absorption and re-emission. Accordingly a metastable state for  $2p$  was postulated. In this case the life of the radiation in the apparatus must depend largely upon the motion of the excited atoms. Approximate calculations based on this assumption agreed well with the experimental facts. The present paper describes experiments made to determine the persistence of  $\lambda 2537$  excited by resonance absorption in a vessel containing mercury vapor, a case in which the process of absorption and re-emission must play an important part. The rate of decay of this radiation excited by striking an arc was also measured.

<sup>1</sup> H. W. Webb, Phys. Rev. 24, 113 (1924).

## METHOD

A photographic method was used. This had a great advantage over the electrical method in that the spectral lines could be studied separately. It had the disadvantage, however, that a large amount of radiation was necessary. The resonance line  $\lambda 2537$  could not be produced below the ionization potential with sufficient intensity and it was therefore necessary to use the radiation  $\lambda 2537$  from an arc for the excitation of the resonance radiation. Thus the complex arc spectrum was always present during the excitation.

The apparatus is shown schematically in Fig. 1. The source *A* was a hot cathode arc in a quartz flask. For the study of the fluorescent radiation excited in a separate vessel, an evacuated quartz cell *B*

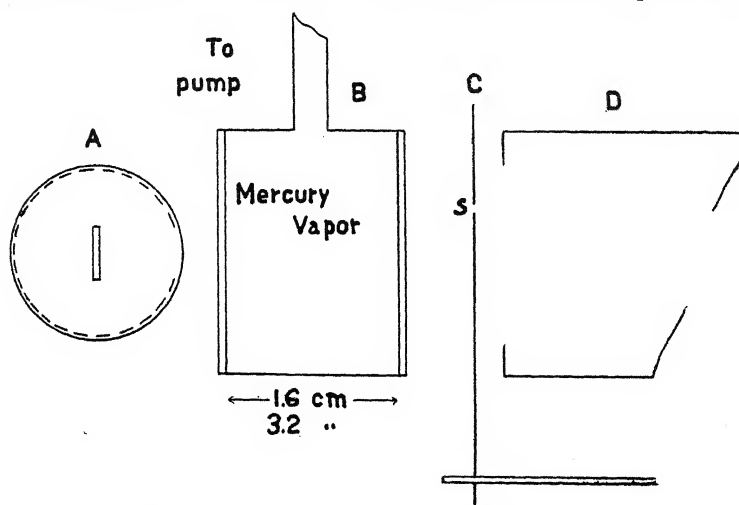


Fig. 1. Arrangement of photographic apparatus.

containing mercury vapor was placed between the source and the quartz spectrograph *D*. A disk *C* having near its circumference a small hole *S* which upon rotation of the disk passed the end of the collimator tube of the spectrograph, acted as a long slit, different parts of which corresponded to different instants of time. This disk was mounted on the axis of a commutator and could be adjusted with respect to the commutator so that the potential exciting the source could be removed at any desired point in the field of view of the spectrograph. The curved trace on the photographic plate beginning at this point revealed the subsequent history of the radiation. The speed of the disk and the law of blackening of the photographic plate were alone needed for quantitative measurement of the rate of decay of the radiation.



## APPARATUS

The mercury arc source was contained in a commercial quartz flask of 150 cc capacity, having a neck, 1.8 cm inside diameter and 9 cm long, sealed with DeKhotinsky cement to a hollow brass plug which was sealed in turn to a glass tube supporting the electrode wires and pumping tube. The flask was mounted in an upright position with a small amount of mercury in the bottom. An electric heater surrounded the bulb. The temperature of the flask was measured by means of a copper-constantan thermocouple attached to the outside of the bulb. The vacuum system consisted of a diffusion pump and forepumps. All observations were made at gas pressures below the limit of a McLeod gauge connected to the flask.

The source of electrons was an equipotential hot cathode of oxide coated platinum. The heating element was of 0.05 mm platinum, and insulated from it by mica was a sheath of 0.16 mm platinum making electrical contact with the heater at one end by a tongue. The sheath was coated with barium and strontium oxides. Heating currents of from 9.5 to 13 amp. were used. Such a cathode gave ample emission at bright red heat and lasted several months under almost daily use with arc currents as high as 2 amp. The anode was a cylinder of nickel gauze, 1.6 mm spacing, 1.8 cm in diameter and 6 cm long. For testing the behavior of the radiation excited in the cells it was necessary to have the arc in a tube of small diameter in order to insure that the radiation from the arc would decay very rapidly upon removal of the exciting potential. The electrodes were, therefore, suspended in the neck of the flask, the anode being in contact with the quartz wall. The radiation passed to the optical system through a slit in the anode.

Since each record on the photographic plate was composed of hundreds of superimposed photographs, it was essential that the commutator and disk be accurately constructed. An excellent commutator was built by the research mechanic, Mr. S. Cooley. The heavy commutator disk, 12.7 cm in diameter and 2.5 cm wide, was divided into 24 sections separated by 0.8 mm of mica, accurately spaced to about .0025 mm. Each section could be connected to either of two slip rings, thus providing for an exciting and a reverse potential. The contacts to the commutator and slip rings were made by hard carbon brushes. The brush on the commutator was ground to a knife edge and placed perpendicular to the surface so that the bearing edge was not more than 0.5 mm wide. The shaft was mounted in ball bearings

and the whole so nicely balanced that it was run for periods of three or four hours without appreciable chattering or heating, even at speeds as high as 70 r.p.s.

The disk *C* was of aluminum, 20 cm in diameter, and was mounted on a steel face plate at the end of the shaft. Corresponding to each pair of commutator sections was a hole (*S*, Fig. 1), 0.3 mm in diameter, the small size being necessary to obtain sufficient resolution in time.

Two cylindrical quartz cells (See Fig. 1) with plane polished ends were used for the study of the radiation excited by resonance. In diameter they were 2.5 cm, and in length 1.6 cm and 3.2 cm, respectively. These cells will be referred to as the short and long cells, respectively. Connection to the vacuum system was provided by a stem in the middle of each. For temperature control this stem was jacketed close to the cell.

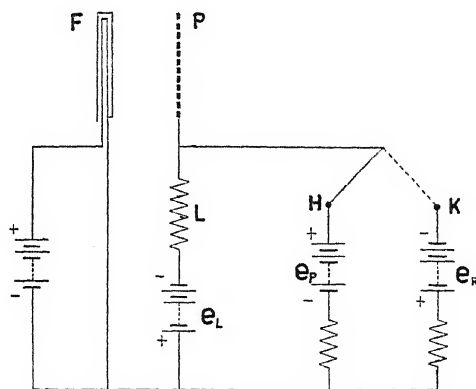


Fig. 2. Electrical circuit of the arc.

#### EXPERIMENTAL PROCEDURE

The essentials of the electrical circuit of the arc are shown in Fig. 2. *P* is the anode and *F* the filament. Two adjacent segments of the commutator are represented by the points *H* and *K*. While *P* was in contact with *H*, usually about  $7 \times 10^{-4}$  sec., the arc was excited by a positive potential  $e_p$ . As the brush passed from the segment *H*, the positive potential was removed from *P*, and after an interval of time corresponding to the passage of the brush over the mica section, the reverse potential  $e_r$  was applied by the segment *K*. The commutator and disk were adjusted so that the positive voltage cut-off came after the hole in the disk had traced a line several millimeters long on the

photographic plate. The exact position of this cut-off was determined from a photograph made while rotating the disk slowly by hand. To test the uniformity of the different parts of the arc, etc., a check photograph with the disk rotating but with an uninterrupted positive voltage on  $P$ , was taken on each plate. This was necessary since patches of unusually intense radiation were occasionally observed in the arc, and there were blemishes in the windows of the quartz cells.

Precautions were taken to eliminate errors due to sparking as the brush left the "live" section of the commutator, and to leakage over the mica insulation. Most of the photographs were taken at arc currents of a few tenths of an ampere, so that with a non-inductive circuit, sparking was reduced until it was barely visible in a darkened room. Again, a leak  $L$ , with or without a reverse voltage  $e_L$ , was introduced to take care of the period during which the brush was on the mica insulation. Also, reverse voltages were maintained on the "dead" commutator sections. Out of at least 50 photographs of the arc alone, some with exposures of several hours, not one gave evidence of faults in commutation. Furthermore, the entire mica insulation corresponded to only 1 mm on the plate, whereas with the long cell in the system the persistent radiation caused a trace 15 mm in length. The effect of vibration of the commutator system with respect to the photographic plate was found to cause an error on the plate of only 0.2 mm, corresponding to an error of less than  $3 \times 10^{-6}$  sec.

Photographs of the arc with electrodes in the neck of the flask were first taken as described above. The quartz cell was then introduced between the arc and the disk and photographs taken as before, using each cell at various speeds of the disk, with temperatures ranging from 40°C to 100°C.

The photographic densities on the plate were measured by means of a small bismuth-silver thermocouple mounted as the cross-hair in a microscope of approximate magnification 2. This magnification, together with the small size of the thermocouple, 1/3 mm by 1/6 mm, gave sufficient resolution for measurements with even the most rapid rate of decay observed.

The photographic densities were translated into intensities by means of test plates developed either in the same bath or under similar conditions. The exposures on the test plates were obtained by photographing a mercury arc of constant intensity for varying intervals of time. The photographs to be measured, on the other hand, were made under the condition of a constant exposure time but varying

intensity. It is well known that for very short times of exposure or for very low intensities the reciprocity law no longer holds, but the work of Harrison and Hesthal<sup>2</sup> shows that for panchromatic films in the wave-length region under consideration the density-log time curves and the density-log intensity curves have the same slope over their linear portions. Only those plates were chosen for measurement, therefore, whose densities lay on the straight part of the density-log exposure curve. When the check photographs, taken with an uninterrupted positive voltage on the anode, showed variation in density over the length of a trace, a correction was applied to reduce to a uniform initial intensity.

#### RESULTS

The intensity-time relation for  $\lambda 2537$  from the arc alone is shown by Curve (a), Fig. 3, starting from the instant of commutation. The intensity of the radiation falls off in a manner approximately exponential with the exponential constant  $1.7 \times 10^5 \text{ sec.}^{-1}$ . This gives the time constant  $0.6 \times 10^{-5} \text{ sec.}$  Besides a strong absorption of  $\lambda 2537$ , the effect of the introduction of the cells into the path of the radiation was to decrease the rate of decay of that line. The longer cell produced the greater change. Curve (b) shows the decay of the radiation for the short cell in the system and Curve (c) that for the long cell. These curves show an approximately exponential decay with the time constants  $4.0 \times 10^{-5} \text{ sec.}$  and  $6.8 \times 10^{-5} \text{ sec.}$  for the short and long cells respectively. These times are roughly proportional to the lengths of the cells. The above curves are each the average of determinations made from several plates, and are not in error by more than 10 to 15 percent.

The persistent radiation from the arc directly transmitted through the cell after the cutting off of the voltage was insufficient to account for the persistence found with the cells. Curve (a) Fig. 3 shows a measurable persistence of  $\lambda 2537$  from the arc, but the rate of decay of this radiation was so rapid that at the time when the radiation measured with the long cell in the path had fallen to  $1/e$  of its initial value, the arc radiation, even if uncorrected for absorption, would have been present with only  $1/7000$  the intensity actually observed. If corrected for the cutting down of the radiation from the arc by the mercury cell, about 98 percent as measured by the relative exposures necessary to give equal plate densities with the arc alone and with the cell in the path, the primary radiation is seen to be entirely negligible

<sup>2</sup> Harrison and Hesthal, Jour. Opt. Soc. of Am., 8, 471, (1924).

after the first  $2 \times 10^{-5}$  sec. As a further check a photograph of the arc was made with the length of exposure necessary to produce a measurable plate with the long cell in the path. The trace on this much overexposed plate had entirely disappeared at a time at which radiation of considerable intensity still persisted with the long cell in the system. These facts show clearly that practically all the persistent radiation coming from the cell was due to some process of absorption and re-emission by the vapor in the cell. The shape of the decay curve for

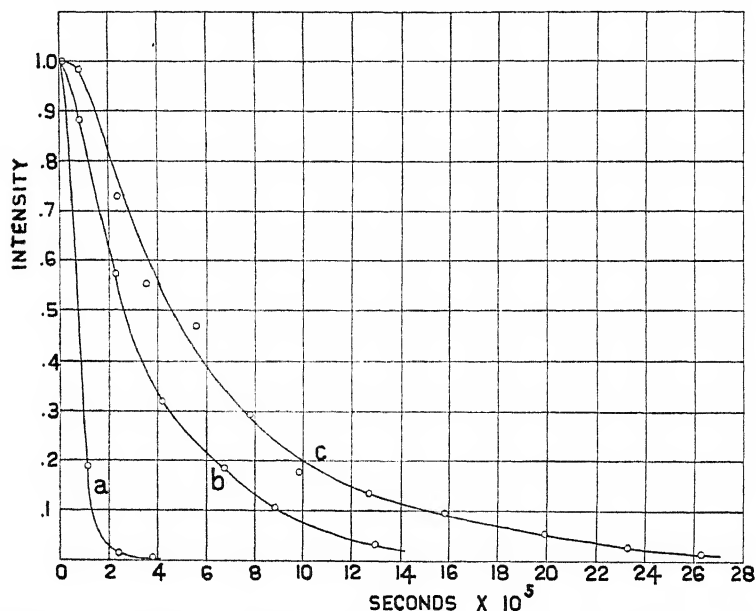


Fig. 3. Rate of decay of  $\lambda 2537$  from the source alone (a) and with the shorter cell (b) and the longer cell (c) in the system.

the first  $2 \times 10^{-5}$  sec. is distorted, however, by the persistent radiation from the arc. No correction can be made, since the method of correction depends upon the unknown processes involved in the persistence.

Over the range of cell temperatures investigated,  $40^\circ$  to  $100^\circ\text{C}$ , the rate of decay of  $\lambda 2537$  was found to be independent of the pressure as measured by the temperature at which the mercury condensed in the stem of the cell. The body of the cell was maintained at a higher temperature to prevent condensation on the faces. Thus the temperature of the liquid mercury in contact with the cell wall was always higher than that of the stem, so that the vapor pressure of the mercury in the cell was higher than that corresponding to the temperature

of the water jacket on the stem. That variation in the vapor pressure in the cell was brought about by the change in temperature of the water jacket is certain, since between the lowest and the highest temperatures employed there was a twenty-fold decrease in the transmission of  $\lambda 2537$ .

It is of interest to note that upon introduction of the cell into the system the increased persistence of  $\lambda 2537$  was observed only when mercury from a drop in the cell was distilling into the stem connected with the vacuum pump. A photograph taken with the cell free from liquid mercury, but connected with the pump so that it contained mercury vapor at about  $30^{\circ}\text{C}$ , showed considerable absorption of  $\lambda 2537$  but no persistence greater than that accounted for by the arc alone. The explanation that at once suggests itself is that the persistence is present only near the surface of distilling mercury. Yao<sup>2</sup> found this condition necessary for the striking of a low voltage arc at 4.9 volts. Doubt is thrown upon this explanation by other photographs taken after the cell had been thoroughly baked, pumped and sealed off. In this case also there was no increased persistence, although mercury was distilling freely into the jacketed stem. It is possible that the condition for the slow decay is not the presence of freshly evaporated mercury vapor, but is the absence of traces of air or water vapor which might have been introduced during the sealing-off process. The cell, containing liquid mercury and connected with the pump, would constitute in itself an effective diffusion pump, so that only extremely pure mercury would be present in the body of the cell. It is well known that a small amount of air is effective in quenching the radiation  $\lambda 2537$  excited by resonance.

#### DISCUSSION

Lack of data relating to the exceedingly complex processes involved in the persistence of radiation in a vapor makes an exact description of these processes impossible at present. The nature of the process of absorption of radiation by an atom and the effect of molecular impact during or after absorption are not understood. The character and the amount of dissipative absorption are not known. In the experiment described above all the lines of the arc spectrum were present during the period of excitation. Since these lines are absorbed by excited vapor it is probable that they play some part in the persistence.

There is reason to expect the presence in the cells of metastable atoms in the  $2p_1$  and  $2p_3$  states, resulting either from impacts of normal

<sup>2</sup> Y. T. Yao, Phys. Rev. 21, 1 (1923).



mercury atoms with excited atoms in the state  $2p_2$  or from the absorption of the strong arc line  $2p_2-1s$  which lifts the electron to the  $1s$  orbit from which two of the three possible transitions leave the atom in the metastable states  $2p_1$  and  $2p_3$ .<sup>4</sup> The effect of impacts with the metastable atoms would be, in part, reversion to the  $2p_2$  state and subsequent emission of  $\lambda 2537$ . There is also the possibility of a mercury molecule formed by impact of a normal atom with an atom in the  $2p_2$  state, although neither the ultra-violet nor green bands characteristic of the fluorescence of mercury at high pressures, and attributed to  $Hg_2$ , appeared on the plates or to the eye.

It is not clear, however, how the persistence of  $\lambda 2537$  may be related to the presence of such metastable atoms in the vapor. One possibly significant fact is, however, to be noted with regard to the above results. The times involved in the rate of decay of  $\lambda 2537$  were of the order of magnitude of the times required for atoms, having the mean velocity corresponding to the temperature used, to traverse the cell without impact. At  $75^\circ C$  the mean velocity of mercury atoms is  $1.9 \times 10^4$  cm/sec. In the case of the cell of length 1.6 cm, an atom would, on the average, traverse a distance equal to the length of the cell in  $8.4 \times 10^{-5}$  sec. For this cell the time constant was  $4.0 \times 10^{-5}$  sec. If, instead of the total length of the cell, the mean length (one-half) is taken, this mean time is  $4.2 \times 10^{-5}$  sec., which is very nearly equal to this time constant. In the case of the long cell the agreement is not so close but the times are still of the same order of magnitude. The experimental curves correspond closely with those calculated on the assumption of a uniform initial distribution of excited atoms throughout the cells and of the passage without impact of these atoms to the walls of the cell, where the energy of excitation is freed as radiation. However, with the vapor pressures used the probability of such a passage without impact is so small that such an explanation of the results by diffusion of excited atoms seems impossible, unless some new factor be assumed such as the compensation of the slower passage of the excited atoms, due to impacts, by the dissipation of the persistent radiation at impact.

Since the whole persistent process depends initially upon the absorption of  $\lambda 2537$ , one would expect at least a part of the persistent radiation to result from repeated absorption and re-emission. Wood has shown that there is such diffusion of radiation in mercury vapor at .001 mm pressure.<sup>5</sup> If this is the only process effective, however,

<sup>4</sup> R. W. Wood, Proc. Roy. Soc. A106, 679 (1924).

<sup>5</sup> R. W. Wood, Phil. Mag. 23, 689 (1912).



the absence of any dependence of the rate of decay on vapor pressure is difficult to account for, unless we may assume some compensating process such as dissipation at impact or a change in the wave-length of radiation emitted during impact. Even at a pressure as low as .001 mm the probability of a quantum of radiation diffusing through the cell without being associated with an atom at impact is small. There is evidence<sup>6</sup> for the dissipative effect of impacts in the decreased intensity of  $\lambda 2537$  excited by resonance absorption in pure mercury vapor at high pressures. At very high vapor pressures the time between impacts may determine the order of magnitude of the persistence, while between the low and high extremes of pressure there is possibly a pressure range over which only a small variation in rate of decay might be observed.

#### PERSISTENT RADIATION FROM A MERCURY ARC

A study of the rate of decay of  $\lambda 2537$  from an arc struck at the center of a mass of mercury vapor, approximately a sphere 6 cm in diameter, was also made. The same quartz flask was used, but the hot cathode and anode were supported at the center of the bulb and a third electrode, a nickel mesh, lined the spherical quartz wall. By a method similar to that employed with the cells, photographs were taken at temperatures from 70°C to 150°C with several voltages on the outer electrode and several different reverse voltages on the anode after commutation.

The curves in Fig. 4 show the rate of decay of  $\lambda 2537$  from this arc. The persistence was very much longer than that observed with the arc in the neck of the flask. The curves are, like those for the cells, approximate exponentials, the time constant in this case being  $5.5 \times 10^{-5}$  sec. The difference between the geometry of the spherical bulb and that of the cylindrical cells makes any comparison involving dimensions very difficult. It is to be noted that the difference of potential between the electrodes after commutation made not the slightest difference in the rate of decay. The same curves were obtained for an open circuit as for reverse potentials from 1 volt to 50 volts. There seems, therefore, little doubt that the persistent radiation  $\lambda 2537$  in the mercury arc was due to the same cause as that in the cells, and is not to be explained by space charge conditions or recombination.

<sup>6</sup> Wood and Kimura, *Phil. Mag.* **32**, 329 (1916).

It is also to be noted that within the limits of experimental error the rate of decay of  $\lambda 2537$  from the arc in the bulb of the flask was independent of the vapor pressure over a range of pressures from .05 mm to 1.7 mm. The curve in Fig. 4 is drawn through points taken from photographs at 78°C, 100°C, and 140°C, as measured by a thermocouple attached to the outside of the bulb near the liquid mercury. Since the seal at the top of the neck of the flask was water cooled, there was considerable condensation at that point, so that the pressure of the mercury vapor was less than that corresponding to the temperature measured. The condensation, however, took place several inches from

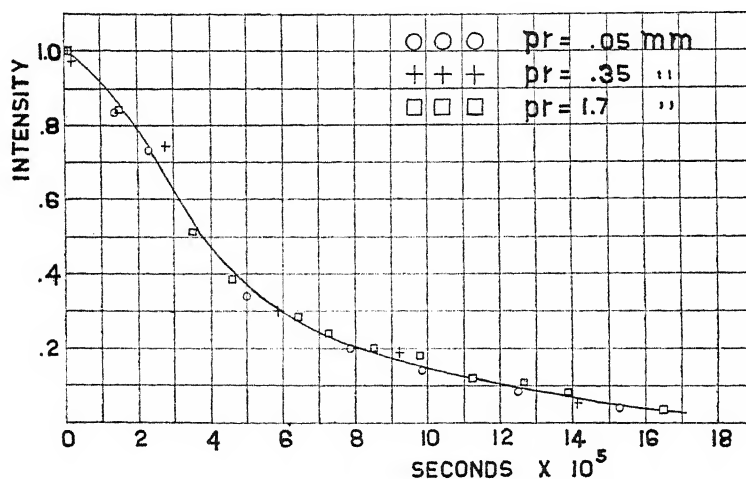


Fig. 4. Rate of decay of  $\lambda 2537$  from the arc in the bulb of the flask.

the top of the bulb, while the electrodes were immediately above the mercury surface. Furthermore, the increase in the intensity of the radiation and the change in the appearance of the arc make it certain that there was a large change in the vapor pressure. The rate of decay was so nearly independent of the vapor pressure that one curve was drawn through the circles, crosses and squares which give the experimental results for vapor pressures, computed as above, of .05 mm, .35 mm, and 1.7 mm, respectively.

At higher temperatures and greater currents the arc emitted after commutation a peculiar many-lined persistent spectrum, which was studied in detail together with the current conditions in the tube after commutation. The results of this study will be discussed in a later paper.

In conclusion I wish to express my indebtedness to Professor H. W. Webb, at whose suggestion and under whose guidance this work was done.

PHOENIX PHYSICAL LABORATORIES,  
COLUMBIA UNIVERSITY,  
May 18, 1925

## DURATION OF FLUORESCENCE OF MERCURY VAPOR

BY R. N. GHOSH

## ABSTRACT

Discussion of experiments by Phillips, Wood and Vanderlingen.—It is suggested that the fluorescence observed with fresh vapor is due to absorption of light by diatomic molecules which thus acquire energy of about 7 volts. The persistence of the fluorescence is accounted for by assuming that many of these activated molecules transmit the energy to others by collisions of the second type, energy which is eventually radiated in several jumps corresponding to the bands observed. If such activated molecules are present, they should ionize Cs and K molecules mixed with them.

1. In a recent paper<sup>1</sup> M. N. Saha and N. K. Sur have pointed out that the chemical and physical activity of nitrogen in the experiments of Lord Rayleigh, can be explained by Klein and Rosseland's theory of collisions of the second type in which a transfer of energy takes place without radiation. According to Saha and Sur the molecules thus acquire energy<sup>2</sup> of 8.2 volts approximately, and the positive bands of nitrogen are due to the quantum emission of this energy by the activated molecules. The persistence of the glow beyond the electrode is due to the fact that all the moving molecules do not lose energy by free radiation but some communicate their energy to non-excited molecules; thus energy is carried beyond the electrodes. It seems to the writer that what we call fluorescence is nothing but an afterglow. In particular, the above explanation can be easily extended to the case of mercury vapor fluorescence as will be shown in this note.

2. Wood,<sup>3</sup> Phillips<sup>4</sup> and others have made an extensive study of the fluorescence of mercury vapor. Phillips observed that if freshly formed vapor of mercury obtained by briskly boiling the liquid be exposed to ultraviolet light, a green fluorescence distills over to the other cooler limb of the inverted U tube. The course could be traced for a length of about eighteen inches (47 cm). The fluorescence spectrum has been recently studied by Wood and J. S. Vanderlingen.<sup>5</sup> Their experiments indicated that only freshly formed vapor shows fluorescence.

<sup>1</sup> Saha and Sur, *Phil. Mag.* (Sept. 1924).

<sup>2</sup> According to others it is about 11 volts.

<sup>3</sup> R. W. Wood, *Phil. Mag.* **18**, p. 247.

<sup>4</sup> Phillips, *Proc. Roy. Soc.* **89**, p. 41.

<sup>5</sup> Wood and Vanderlingen, *Astrophys. J.* (Oct. 1921) p. 152.

The absorption spectrum of Hg vapor at high vapor density consists of (1) an asymmetrical band with a head at  $\lambda 1849$  which gradually creeps towards longer wave-lengths; (2) four lines, 2346, 2339, 2334, and 2331, which fuse together with rise of temperature forming a band which gradually pushes towards the shorter wave-lengths, and (3) a strong absorption band with head in close proximity to the line 2539.

With zinc spark excitation the fluorescence spectrum consists of (1) a structureless symmetrical band extending from the red down to the wave-length 3700, with its maximum at about 4850; (2) a symmetrical band with a maximum at about 3300, and (3) two small fluorescence bands with maxima at about 2539 and 2346 respectively. Restricting the exciting light to a definite wave-length by means of a monochromator, the aluminum line 1854 gave a fluorescence spectrum consisting of the green violet band (maximum at 4850). The authors<sup>5</sup> then tried zinc lines 2024, 2061, 2909 and 2138 by turns as the exciting light, and the fluorescent spectrum was found in each case to consist of the same green violet band, the ultraviolet band, and a faint band at about 2349. The authors conclude from these and other results that the absorption band 1849 is a complex one, so that excitation by various lines in that region is capable of producing fluorescence.

Neither the absorption nor the fluorescence due to lines below 1849 has been studied, but it can be concluded that when the exciting light is in the neighborhood of 1849, the fluorescing bodies must have absorbed the energy corresponding to that light and fluorescence with the emission of that energy. The energy corresponding to 1849 is about 6.7 volts. From the nature of the absorption bands and the fact that fluorescence does not occur in a cooling vapor but only with a freshly formed vapor,<sup>2</sup> it is concluded that the fluorescing molecules must be of the simplest type, that is diatomic. The exciting light from aluminum or zinc has no relation to the series spectrum of the atomic vapor. Hence, the formation of diatomic molecules cannot be attributed to an excited state of the atoms. The unstable diatomic molecules are given off<sup>6</sup> by the liquid when the temperature is either rising or constant. These molecules by the absorption of energy are brought into an activated condition; that is the energy of each molecule increases by about 6.7 volts. This energy is radiated out in jumps corresponding to 4850, 3300, and 2346. Wood<sup>3</sup> has shown that the fluorescent vapor is transparent in the ultraviolet region,

<sup>6</sup> A discussion will be found in "Origin of Spectra" by Foote and Mohler, p. 106, and Sommerfeld, English edition, p. 440.

a fact which lends support to the above view about the activated state of the molecules.

It is now an established fact that band spectra are due to molecules. There are three types of energy associated with energy of radiation by a molecule, (1) the electronic energy, (2) the energy of atomic vibration, and (3) that of the rotation of the molecule as a whole. Corresponding to the three types of activation we have three types of spectra. When energy of type (1) is quantized we obtain broad bands, say 100-300Å wide; type (2) when quantized gives rise to bands 5-10Å wide, while type (3) gives rise to the fine structure of the bands corresponding to type (2). Now in the case of the fluorescence spectra of mercury vapor we have seen that continuous bands with maxima are obtained. The continuity of the band on the longer wave-length side beyond the maximum is a departure from the general rule. This is probably due to the frequency of the mutual collisions between two molecules, resulting in intramolecular change of the electrons.<sup>7</sup> The maxima 2346, 2539, 3300 and 4850 may be considered to be the steps by which the quantized energy is radiated.

The prolongation of the path of the fluorescent vapor in Phillip's experiments can be explained on the present view of the activated state of the molecules. Ordinarily, when mutual collisions between atoms in the activated state and those not excited, are not very probable, the energy is freely radiated out by the excited ones after  $10^{-8}$  sec. Wood<sup>8</sup> has recently measured the time interval between the excitation and the appearance of fluorescence of Hg vapor, and found it to be of the order of  $6 \times 10^{-5}$  sec. Total duration of fluorescence is of the order  $3 \times 10^{-4}$  sec. The duration of the excited state of the molecules of Hg vapor will be of the same order; hence, if there was no collision between an activated molecule and a non-activated molecule, the duration of fluorescence or the path of the moving vapor in the fluorescent state cannot be very long. But the high vapor density increases the possibility of collisions of the second type to a great extent, and hence the whole column in Phillips' experiment is filled up with glow, due to the free radiation by a part of the activated molecules, the remainder transferring their energy to non-excited molecules, thus carrying the energy far from the excited region.

Wood's<sup>9</sup> observation that the intensity of fluorescence of iodine molecules is diminished by the addition of fresh iodine molecules, can be

<sup>7</sup> See Lenz, *Phys. Zeits.* 21, p. 691 (1920).

<sup>8</sup> R. W. Wood, *Proc. Roy. Soc.* vol. 99.

<sup>9</sup> R. W. Wood, *Researches in Physical Optics*, p. 80.

easily explained on the above view. What happens is that when fresh molecules are added the probability of collision increases, and therefore the activated molecules transfer their energy to non-excited molecules. Hence, the amount of free radiation at any instant diminishes.

We have seen that the fluorescent mercury vapor is loaded with energy of 6.7 volts; hence, when these molecules are mixed up with caesium or potassium vapor they should be ionized, since the ionization potentials of these are below 6.7 volts.

The author gratefully acknowledges his deep thanks to Prof. M. N. Saha for his interest and help.

PHYSICS DEPARTMENT,  
ALLAHABAD UNIVERSITY, INDIA.  
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Note added in proof. Since the above was sent for publication Lord Rayleigh's experiments (Proc. Roy. Soc. 108, 262, 1925) throw more light upon the phenomenon. The absence of  $\lambda$  1850 (1S-1P) in the distilled vapor, though strong in the arc, supports the view expressed above. The exercised diatomic (unstable) molecule under the conditions of the experiment, dissociates into one activated (4.7 volts) and one non-activated atom, the former radiating  $\lambda$  2537 (1 $p_2$ -1S). This view is supported by the fact that the electric field does not quench the line, since it originates from neutral molecules. It seems, therefore, that the energy of dissociation of the diatomic molecules is less than 2 volts. The presence of some lines in the distilled vapor is due to the activation of the atoms by collision with the energized molecules. No lines appear whose energy level is greater than 7 volts.



THE OPTICAL CONSTANTS OF MAGNESIUM  
AND ZINC CRYSTALS

BY M. E. GRABER

## ABSTRACT

Magnesium and zinc were prepared in the form of hexagonal crystals. Their optical constants (4500A to 6500A) were then determined by the crystalliptometer, polarimetric method. Plane polarized light at an azimuth of  $45^\circ$  was reflected from one of the six faces of the crystal which was placed successively in two principal positions in which the principal axis of the crystal was (1) perpendicular or (2) parallel to the plane of incidence. Two sets of optical constants (index of refraction, absorption index and reflecting power) were thus obtained for each metal. Both indices of refraction for magnesium were found to be less than .5 for wave-lengths within the visible spectrum. The indices of refraction for zinc were found to be greater than unity except for the shortest wave-lengths employed. The reflecting powers of both metals agree well with the comparison determinations available. No marked selectivity was found in the optical properties of either metal.

## INTRODUCTION

THE most consistent values of the optical constants of metals have been obtained from analysis of the elliptically polarized light reflected from their surfaces. If the resultant elliptic vibration is resolved into components parallel and perpendicular to the plane of incidence, it is possible to compute the optical constants of the reflecting metal in terms of the amplitude ratio and the relative phase difference of these two components by means of Drude's formulas.

The first application of this method to absorbing crystals was made by Drude<sup>1</sup> and by Mueller<sup>2</sup> on lead and antimony sulfides which occur in nature as crystals.

Professor L. P. Sieg suggested that crystal elements be prepared to eliminate as far as possible errors due to different degrees of polish and heterogeneity of surface. Working under his direction, L. D. Weld,<sup>3</sup> C. H. Skinner,<sup>4</sup> G. D. Van Dyke,<sup>5</sup> and R. F. Miller<sup>6</sup> have

<sup>1</sup> P. Drude, Wied. Ann. 34, 489 (1888).

<sup>2</sup> H. Mueller, Dissert. Gottingen (1903).

<sup>3</sup> L. D. Weld, J. Opt. Soc. Am. 6, 67 (1922).

<sup>4</sup> C. H. Skinner, Phys. Rev. 9, 148 (1917).

<sup>5</sup> G. H. Van Dyke, J. Opt. Soc. Am. 6, 919 (1922).

<sup>6</sup> R. F. Miller, Thesis, University of Iowa, (1923).

studied the optical properties of selenium and tellurium, and obtained reasonably consistent results for all the optical constants involved.

The object of the present study was to determine the two sets of optical constants of magnesium and zinc crystals within the wavelength limits 4550Å to 6500Å.

#### EXPERIMENTAL METHODS

The magnesium crystals were supplied by S. L. Hoyt of the General Electric Company, and W. A. Scheuck of the Western Electric Company. The zinc crystals were produced by three methods, (1) by breaking cylindrical zinc castings, (2) by melting zinc in an electric furnace

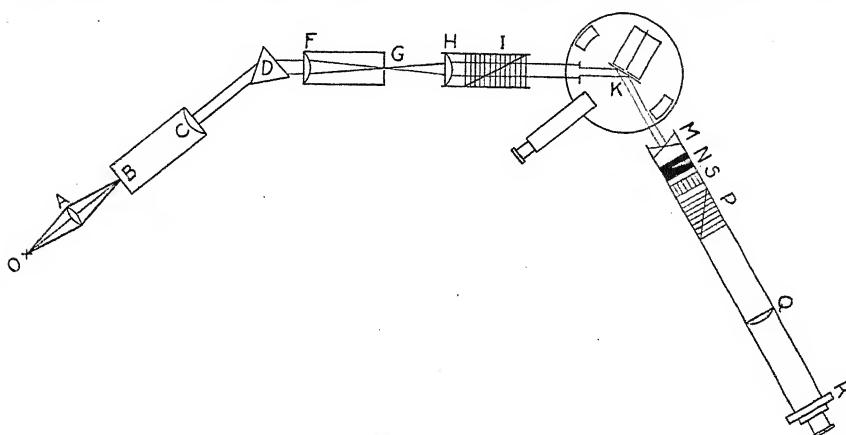


Fig. 1. Diagram showing arrangement of monochromator and crystalliptometer.

and attempting to draw it out as single crystals by means of a glass rod, (3) by permitting molten zinc to cool in a quartz tube and breaking the cast. In no case was a single crystal produced, but fracture yielded occasional lateral faces of a crystal.

The apparatus employed for light production and analysis consisted of an 11-ampere tungsten ribbon lamp *O*, a condensing lens *A*, a Hilger monochromator (type D32) *BCD*, a collimator *FG*, a crystal mount *K* and the crystalliptometer *M-R*, arranged as in Fig. 1.

After leaving the slit *G*, the beam of light passes through a focusing lens *H* and a pair of quartz wedges *I*, fixed with reference to each other. The optical axis of the wedge nearest the observer is vertical, while that of the second wedge is horizontal. Since the light vector perpendicular to the optic axis is faster than the other component, the vertical component of the incident light is slower for points to the left of the center line of the compensator while the horizontal component

is faster for all points to the right of the center line. The phase difference  $\Delta$  at a distance  $x$  from the center is  $cx + \nabla$  where  $c$  is the compensator constant and  $\nabla$  the original phase difference. The result is plane polarized light where  $cx + \nabla = \text{zero}, \pi, 2\pi$ , etc. Great care was taken in the selection of crystals to insure a definite structure and one plane lateral surface. The crystal was mounted so that the plane of its face remained unchanged upon rotation through  $90^\circ$  about an axis perpendicular to that plane.

When the beam of plane polarized light at  $0^\circ$  incidence was reflected from the metallic surface the only effect was a rotation of the plane of polarization through  $90^\circ$  and we then had plane polarized light with an azimuth of  $135^\circ$  relative to the  $X$ -axis. Any change made in the angle of incidence produced a change of phase so that the reflected light became elliptically polarized.

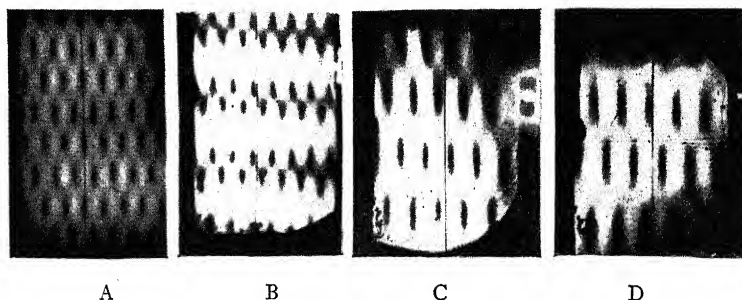


Fig. 2. Typical spot patterns

- A. Direct transmission comparison plate, 4550A.
- B. Tellurium pattern, 4960A.
- C. Magnesium pattern, 6200A, horizontal position.
- D. Zinc pattern, 6300A, horizontal position.

The crystalliptometer constructed by Dr. L. D. Weld consists of (1) a reticule  $M$  with vertical cross hair, (2) a rotator  $S$  consisting of a right and a left hand wedge the optical axis of each being in line with the direction of transmission, (3) a Glan-Thomson nicol  $P$ , (4) a converging lens  $Q$ , and (5) a photographic plate holder  $R$ . In passing through the rotator the periodically recurring bands of plane polarized light are rotated through an angle measured by  $ky$  where  $k$  is the rotation constant and  $y$  the displacement. The nicol interposed at  $P$ , Fig. 1, extinguished the vertical component of the beam. Wherever a plane polarized beam vibrating vertically exists, light cannot pass and dark spots result. When the light is elliptically polarized or has a horizontal component it will pass through the nicol and produce

an effect upon a photographic plate. The result on the plate is a spotted pattern the design of which depends upon the character of the elliptically polarized light. By comparing the spot-patterns for direct transmission with the corresponding patterns for light reflected from the crystal surface it is seen that each spot is shifted vertically and horizontally. See Figs. 2-5.

Fig. 2A represents the photographic image produced by plane polarized light passing directly through the wedge-systems of the rotator and the analyzer. The intersections of the vertical bands of plane polarization and the horizontal bands of  $90^\circ$  azimuth, are the spots of zero light intensity distributed in an approximately symmetrical order relative to the vertical cross hair.

In Fig. 2B the elliptic polarization of the light reflected from the plane face of a tellurium crystal has produced a displacement of all the spots of zero intensity in the same direction along the horizontal bands of equal azimuth and corresponding row displacements along the vertical bands of equal phase difference, but alternately in opposite directions. The bunching of rows is more clearly indicated in Fig. 2B than in the case of either magnesium, Fig. 2C, or zinc, Fig. 2D.

In measuring the photographic plates to determine the vertical spacing of the rows and the horizontal shift of the columns of spots from the position of phase difference  $\Delta = \Pi$ , a Gaertner 50 cm comparator was employed. Having marked the plate before photographing by placing it in a holder with small apertures and exposing to a light flash, it was placed upon the stage of the measuring microscope with the film side up.

Having adjusted the comparator so that the cross hair bisected the first row of spots, the micrometer screw was turned and readings taken for each row from the top to the bottom of the plate. The average of the shorter spacings was then found and designated  $q$ .

The same method was employed in measuring  $d$  the horizontal distance between successive spots and  $a$ , the horizontal shift of the columns of spots to the right of  $H$ .

#### HORIZONTAL SPOT PATTERN

$H$						
1	2	3	0	4	5	6
0	0	0	0	0	0	0
0	0	0	0	0	0	0
7	8	9	10	11	12	

Let  $x_0, x_1, x_2, \dots, x_n$  be the absolute distances of the spots  $0, 1, 2, \dots, n$  from  $H$ .

Then  $x_0 = a$ ;  $x_3 = d - a$ ;

$$x_1 + x_2 + x_3 = 3d + 3(d - a) = 6d - 3a; \quad (1)$$

$$x_4 + x_5 + x_6 = 6d + 3a; \quad (2)$$

$$x_7 + x_8 + x_9 = 3d + 3(\frac{1}{2}d - a) = 4\frac{1}{2}d - 3a; \quad (3)$$

$$x_{10} + x_{11} + x_{12} = 3d + 3(\frac{1}{2}d + a) = 4\frac{1}{2}d + 3a; \quad (4)$$

Adding (1), (2), (3) and (4)

$$x_1 + x_2 + \dots + x_{12} = \Sigma x = 21d; \quad d = \Sigma x / 21. \quad (5)$$

Subtracting (1) + (3) from (2) + (4)

$$12a = (x_4 + x_5 + x_6 + x_{10} + x_{11} + x_{12}) - (x_1 + x_2 + x_3 + x_7 + x_8 + x_9). \quad (6)$$

A comparison photographic plate was taken with the crystelliptometer in direct alignment with the collimator (Fig. 2A). Measurements of this plate determined the position of  $H$ , the value of  $d$ , and the vertical column spacing  $p$ .

The largest errors in the measurements of  $a$  and  $q$  are due to the difficulty in finding the true centers of area of the spots. Various methods of reducing these errors have been suggested but the variation in size and in spot intensity renders any one method inadequate. The value of  $d$  is more accurate when taken from the measurements on the comparison plate, since the spots are of more uniform size and the pattern more distinctly clear cut than in the plates taken with reflected polarized light. Large differences in the value of  $d$  indicated inaccurate measurements.

#### DRUDE'S FORMULAS

If  $\Delta$  represents the difference in phase and  $\Psi$  the change in azimuth of the two components of reflected light,

$$\pi - \Delta = (a/d) \ 360^\circ \quad (7)$$

where  $a$  is the shift of each column of spots from the position for  $\Delta = \pi$  and  $d$  is the distance between columns.

$$\text{Again} \quad \Psi = (q/p) \ 90^\circ \quad (8)$$

where  $q$  is the distance between adjacent rows of spots after reflection from the crystal surface and  $p$  is the corresponding distance before reflection.

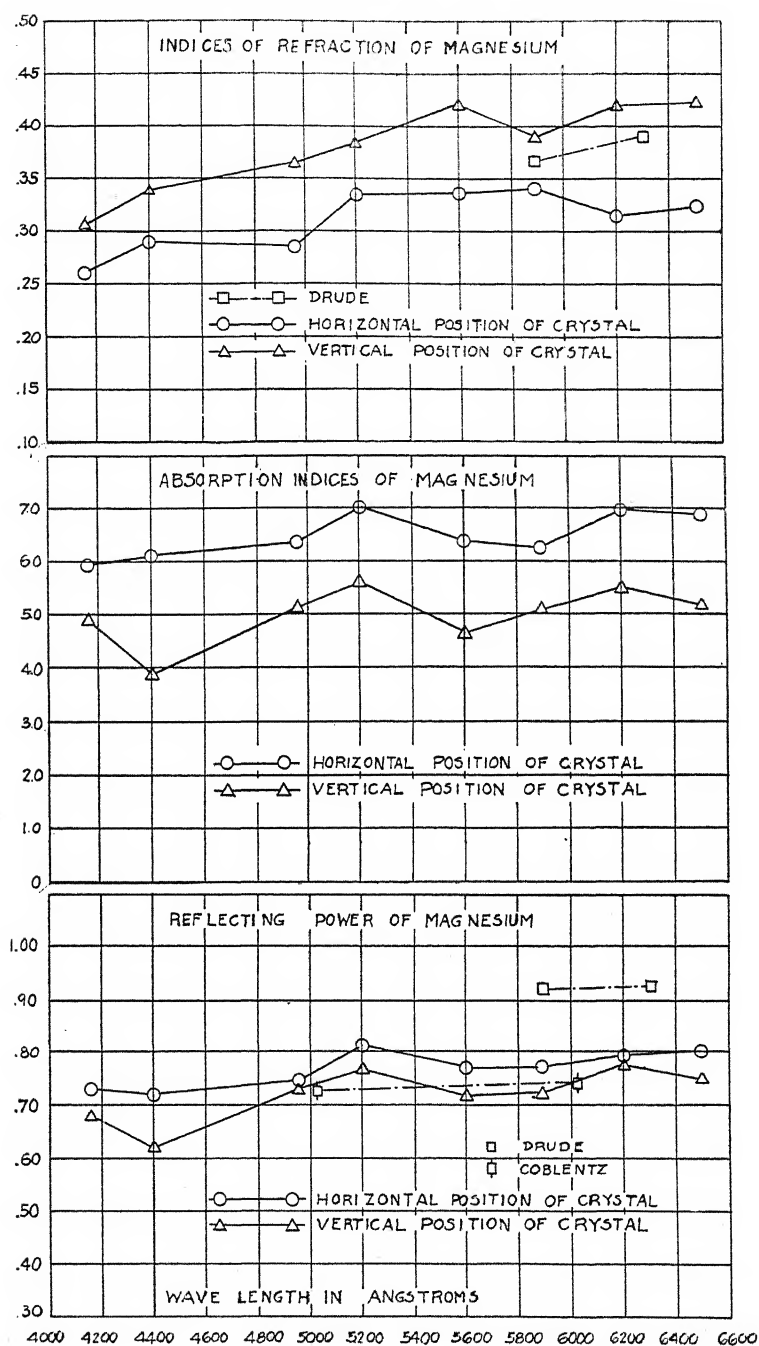


Fig. 3. Optical constants of magnesium.

In determining the optical constants of the crystal with its principal axis perpendicular and parallel respectively to the plane of incidence, the formulas used by Drude<sup>7</sup> and by Mueller were applied.

### RESULTS

With the angles of incidence ranging from 60° to 80°, the two sets of averaged optical constants obtained for magnesium are given in Table I.

TABLE I  
*Optical constants for magnesium*

Wave-length	$N_1$	$N_2$	$K_1$	$K_2$	$R_1$	$R_2$
4160A	.260	.305	5.95	4.94	.730	.680
4400	.290	.340	6.10	3.87	.720	.620
4960	.285	.365	6.37	5.06	.745	.715
5200	.335	.385	6.97	5.57	.810	.765
5600	.337	.420	6.38	4.62	.785	.715
5890	.340	.390	6.25	5.05	.785	.722
6200	.315	.420	6.97	5.48	.795	.775
6500	.323	.423	6.94	5.18	.800	.745

The above results are plotted in Fig. 3.

The only values of optical constants for magnesium available for comparison purposes are those of Drude and of Coblenz. The indices of refraction for the vertical position of the magnesium crystal are in close agreement with Drude's results for polished magnesium surfaces. There is, however, a marked departure from Drude's results for absorption indices and reflecting powers. He obtained 11.8 as the absorption index of magnesium for wave-length 5890A, which results in the abnormally large reflecting power of 93 percent. Coblenz by direct measurements determined the reflecting power of magnesium to be approximately 72 percent for the same wave-length, which is within a few percent of the tabular values above. Toole's<sup>8</sup> observations indicate that Drude's high absorption was due to the surface mat developed by polishing. The magnesium crystals employed in this investigation lost their reflecting power in the course of a few weeks, and new crystals were substituted. Drude, Tate, and Toole agree that polishing increases the reflection and absorption coefficients of metals although the forms of the curves for the optical constants are not materially changed by polishing or by impurities. Tyndall<sup>9</sup> also found that although there was

<sup>7</sup> Drude, *Ann. der Physik* **32**, 584 (1887).

<sup>8</sup> Toole, *Phys. Rev.* **31**, 1 (1910).

<sup>9</sup> E. P. T. Tyndall, *Phys. Rev.* **21**, 162-181 (Feb. 1923).



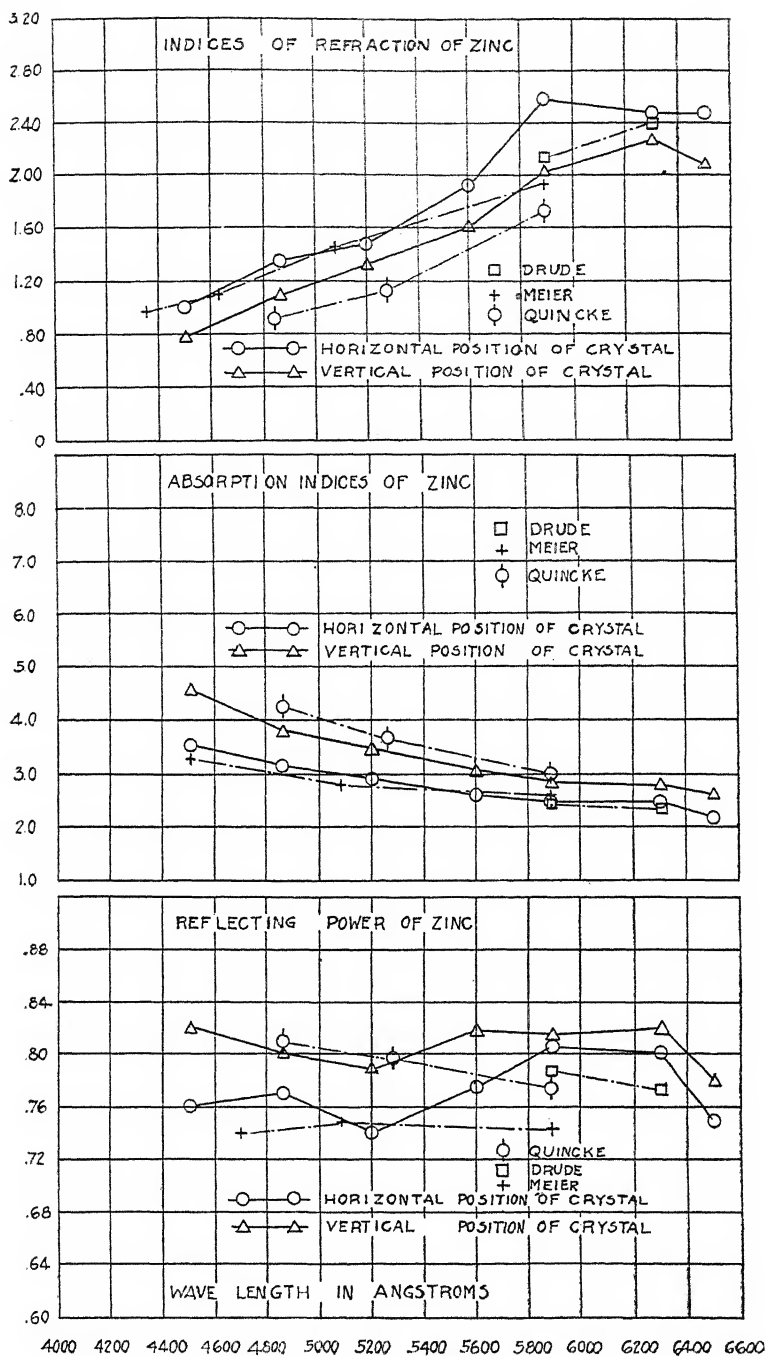


Fig. 4. Optical constants of zinc.

no agreement between his values of  $K$  in the case of molybdenite and those of Crandall, the general trend of their curves was the same.

The corresponding optical data for zinc are exhibited in Table II.

TABLE II  
*Optical constants for zinc*

Wave-length	$N_1$	$N_2$	$K_1$	$K_2$	$R_1$	$R_2$
4550A	1.00	.78	3.55	4.58	.760	.820
4860	1.35	1.09	3.14	3.80	.770	.800
5200	1.47	1.32	2.94	3.49	.740	.790
5600	1.92	1.61	2.60	3.08	.775	.820
5890	2.58	2.02	2.29	2.86	.805	.815
6300	2.47	2.27	2.47	2.79	.800	.820
6500	2.47	2.07	2.15	2.60	.750	.780

The above results are plotted in Fig. 4.

The optical constants of zinc have been determined for 5893A and 6300A by Drude, for the range from 4310A to 6500A by Quincke, and for the range from 4413A to 6680A by Meier. Comparison of the results in Table II with those of the above authorities indicate that the writer's indices of refraction for the vertical position of the crystal lie between those of Quincke<sup>10</sup> and of Meier<sup>10</sup> for the range from 4550A to 5890A and below those of Drude<sup>10</sup> between 5890A and 6300A. The corresponding indices of refraction for the horizontal position of the crystal are larger than those of any other authority cited. The absorption indices for the horizontal position of the crystal compare well with those obtained by Meier<sup>10</sup> and by Drude while the corresponding indices for the vertical position of the crystal are reasonably close to those of Quincke.

The reflecting powers for both the horizontal and vertical positions of the zinc crystal are greater than any other available results beyond 5700A. The reflecting power for the horizontal position varies from 74 percent to 80 percent and for the vertical position from 78 percent to 82 percent. The higher reflecting powers obtained for the zinc in the crystal form are probably due to the fact that the crystal possesses nearly filmless and homogeneous surfaces along each of the principal directions, with distinctive optical properties depending upon the relative position of the axis and the angle of incidence. The drop in reflecting power at 6500A may be the beginning of a deep minimum observed by Coblentz<sup>11</sup> at 10,000A.

<sup>10</sup> Landolt-Bornstein-Roth Tabellen.

<sup>11</sup> Coblentz, Bur. Stds. Sci. Papers, No. 379, 16, 251 (1920).

In conclusion the writer wishes to express his appreciation to the Physics Department of the University of Iowa for assistance rendered, especially to Prof. L. P. Sieg under whose direction the work was carried on, and also to acknowledge indebtedness to Dr. E. O. Hulburt for the use of his lenses and filters.

UNIVERSITY OF IOWA,  
IOWA CITY, IOWA,  
March 3, 1925.

THE ORIENTATIONS OF CRYSTALS IN  
ELECTRODEPOSITED METALS\*

BY RICHARD M. BOZORTH

## ABSTRACT

If a metallic film is placed in the path of a circular beam of x-rays, the Debye-Scherrer circles obtained on a photographic plate will each be nearly uniform in intensity if the crystals are oriented at random. If the circles contain spots of greater intensity, certain crystal planes must be oriented so as to make an average angle  $\alpha$  with the normal to the film. (1) A *graphical method of determining the orientations* is described, a modification of that given by Polanyi and by Uspenski and Konobejewski, together with charts of the values of  $\alpha$  corresponding to the location of intense spots for three values of the angle  $\beta$  of the beam with the normal to the film, and also a table of the values for  $\alpha$  for different planes for the cubic system. (2) *Electrodeposited films of copper, zinc and cadmium* were found to have crystals oriented at random, but *films of iron, nickel and cobalt* show special orientations. For Fe, the (111) planes tend to lie parallel to the surface; for Ni the (100) or (211) planes tend to be parallel to the surface. The orientation was less marked for Co and only slightly evident for *silver*. In the case of Ni, the degree of special orientation was found to increase with the thickness of the films studied (2 to  $130 \times 10^{-4}$  cm) and at the same time the size of some of the crystal grains greatly decreased, reflecting more general radiation. A magnetic field had no influence on the amount of orientation. (3) *Association of the effect with strain in the films*. It is known that electrodeposited films are in a state of stress, presumably because of the hydrogen deposited with the metal, and that strained metals tend to have oriented crystals. It is suggested, therefore, that the orientation in this case is associated with the strain developed during deposition.

## 1. INTRODUCTION

THE crystalline structures of rolled metals and hard-drawn wires were first explained by Polanyi, Weissenberg, Mark and Ettisch,<sup>1</sup> independently by Uspenski and Konobejewski,<sup>2</sup> and more recently by Jeffries<sup>3</sup> and others. All of these observers deduced from x-ray photographs the distribution in angle of the principal crystal axes in the minute grains constituting these substances. This paper describes a

\* Reported in part at the Washington Meeting of the American Physical Society, April 25, 1924. (See abstract in Phys. Rev. 23, 764, June 1924).

<sup>1</sup> See especially M. Polanyi, Zeits. f. Phys. 7, 149-180 (1921); K. Weissenberg, Ann. der Phys. (4) 69, 409-435 (1922); M. Polanyi and K. Weissenberg, Zeits. f. techn. Phys. 4, 199-208 (1923).

<sup>2</sup> N. Uspenski and S. Konobejewski, Zeits. f. Phys. 16, 215-27 (1923).

<sup>3</sup> Z. Jeffries, Trans. Am. Inst. Min. Eng. 70, 303-327 (1924).

similar study of the orientations of the crystals in electrolytically deposited metals, those examined being Fe, Co, Ni, Cu, Zn, Ag and Cd.

## 2. METHOD OF X-RAY EXAMINATION

The metals were examined in the form of foils. These were deposited on cathodes of polished copper or iron which, just before the deposition, were coated with a thin film of selenium, making it easy to strip the foil from the cathode for subsequent examination. The foil was now mounted in the path of a beam of x-rays of circular cross section. The x-rays were supplied by a molybdenum target water-cooled tube, run at 40 kv peak, and were filtered through a zirconia screen. The photographic plate (Eastman X-Ray 5"  $\times$  7") was placed 5 cm behind the sample, perpendicular to the incident beam.

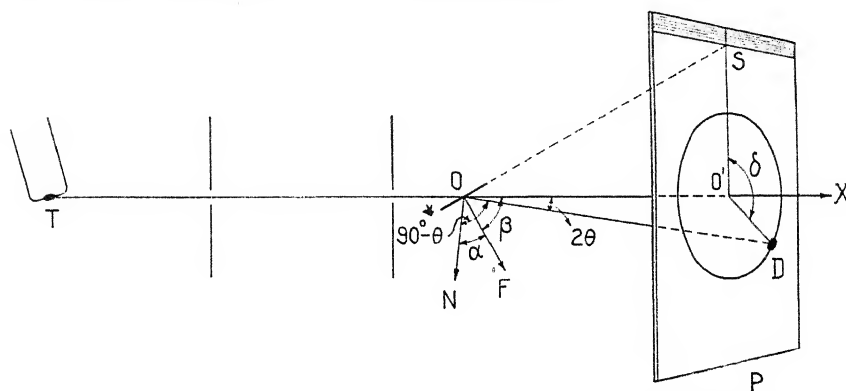


Fig. 1. Diagram showing refraction of beam to photographic plate *P*.

If the crystals in the foil were oriented at random each of the usual Debye-Scherrer circles would be of uniform intensity around its circumference except for the effect of absorption in the foil, which, in general, would be different for different directions of emergence and would produce differences of intensity between widely separated points. Regions of conspicuous intensity, such as those seen in Fig. 5, indicate, therefore, the existence of a special orientation of the individual crystals. In electrolytic foils it is to be expected that the distribution of equivalent crystallographic directions will have axial symmetry about a line perpendicular to the foil; that this is true is proved by the fact that when the foil is perpendicular to the beam each Debye-Scherrer circle is of uniform intensity around its circumference, although the consecutive circles have relative intensities greatly different from those known to correspond to random distribution.

In Fig. 1, the x-ray beam  $TX$ , cuts the sample at  $O$  and the photographic plate at  $O'$ ;  $OF$  is the normal to the surface of the sample on the side from which the primary beam emerges;  $ON$  is the normal to the family of atom-planes which reflects x-rays in accordance with the equation  $n\lambda = 2d \sin \theta$  on to the photographic plate  $P$  at  $D$ ; the line  $O'S$ , chosen for reference, lies in the plane  $P$  and in the plane  $O'OF$ , on the opposite side of  $OO'$  from  $OF$ . The following relation<sup>1,2</sup> then exists between the angles marked in Fig. 1

$$\cos \alpha = \cos \beta \sin \theta + \sin \beta \cos \theta \cos \delta.$$

Of these quantities,  $\theta$  is known from the crystal structure and the wavelength of the x-rays, and  $\delta$  is measured on the plate;  $\beta$  can be determined most accurately from the relation  $\tan \beta = OO'/O'S$ , where  $OO'$  is calculated from the measured distances  $O'D$  and the known values of  $\theta$ ,

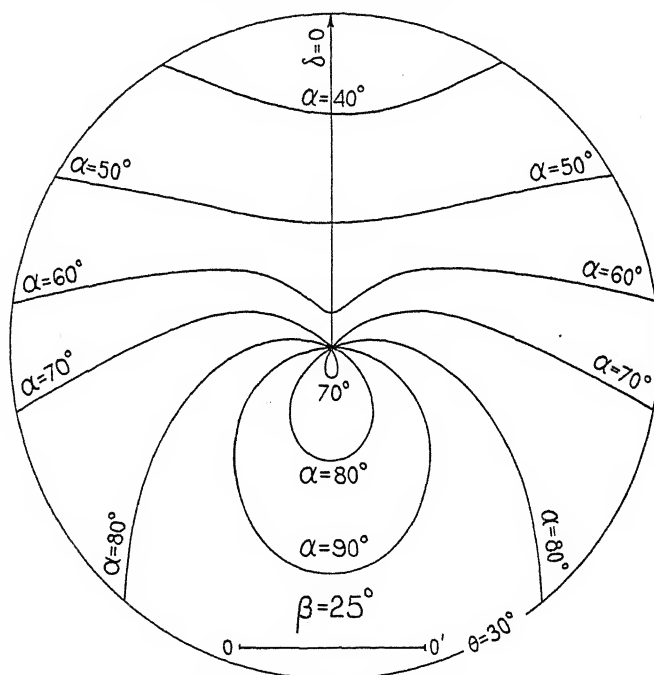


Fig. 2. Chart showing lines of constant  $\alpha$  for  $\beta = 25^\circ$ .

and  $O'S$  is the distance on the plate from the central image to the edge of the unexposed streak on the plate due to the maximum absorption of scattered radiations in the plane of the sample.

In practice, the crystallographic direction  $[hkl]$  which coincides with the normal to the foil, is determined with the aid of a chart and a

table. The chart is constructed for the chosen value of  $\beta$ , a different chart being required for each inclination of the foil to the beam. For any arbitrary value of  $\alpha$  a curve is drawn giving  $\delta$  as a function of  $\theta$ , where  $\delta$  is plotted in azimuth and  $\theta$  is plotted radially in such a way that a line of constant  $\theta$  is a circle having the radius  $OO' \tan 2\theta$ , the radius of the Debye-Scherrer circle produced on the plate by x-rays reflected from crystal planes inclined at the angle  $\theta$  to the incident beam (see Fig. 1). The chart is completed by drawing in a similar manner curves for other values of  $\alpha$  chosen to facilitate interpolation, e. g. at intervals of  $10^\circ$ . Charts for several values of  $\beta$  ( $25^\circ$ ,  $50^\circ$ ,  $75^\circ$ ) are shown in Figs. 2, 3, and 4, and may be copied for use in determinations of this kind by so enlarging them that the length of the line labeled  $OO'$  is equal to the distance from the sample to the photographic plate.

In using a chart to determine  $\alpha$ , the photographic plate is placed over it and values of  $\alpha$  read off for each point of maximum intensity on each Debye-Scherrer circle. A table is now constructed giving the angles between simple planes of the same or different indices. Table I has been so constructed for the cubic system. For the Debye-Scherrer circle produced by reflection from planes whose indices are  $(HKL)$ , the planes  $(hkl)$  are found for which the angles tabulated are equal to the values of  $\alpha$  just determined. Repeating the process for the other Debye-Scherrer circles, the crystallographic plane  $(hkl)$  which coincides with the plane of the foil is, in general, uniquely determined and the determination confirmed.

TABLE I

*Angles between crystallographic planes in crystals of the cubic system.*

( <i>HKL</i> )	( <i>hkl</i> )	Values of $\alpha$ , the angle between ( <i>HKL</i> ) and ( <i>hkl</i> )				
100	100	0°	90°			
	110	45°	90°			
	111	54°44'				
	210	26°34'	63°26'	90°		
	211	35°16'	65°54'			
	221	48°11'	70°32'			
	310	18°26'	71°34'	90°		
	311	25°14'	72°27'			
	320	33°41'	56°19'	90°		
	321	36°43'	57°42'	74°30'		
110	110	0°	60°	90°		
	111	35°16'	90°			
	210	18°26'	50°46'	71°34'		
	211	30°	54°44'	73°13'	90°	
	221	19°28'	45°	76°22'	90°	
	310	26°34'	47°52'	63°26'	77° 5'	
	311	31°29'	64°46'	90°		
	320	11°19'	53°58'	66°54'	78°41'	
	321	19° 6'	40°54'	55°28'	67°48'	79° 6'



TABLE I—continued

*Angles between crystallographic planes in crystals of the cubic system.*

(AKL)	(hkl)	Values of $\alpha$ , the angle between (HKL) and (hkl)							
111	111	0°	70°32'						
	210	39°14'	75° 2'						
	211	19°28'	61°52'	90°					
	221	15°48'	54°44'	78°54'					
	310	43° 5'	68°35'						
	311	29°30'	58°31'	79°58'					
	320	61°17'	71°19'						
	321	22°12'	51°53'	72° 1'	90°				
210	210	0°	36°52'	53° 8'	66°25'	78°28'	90°		
	211	24° 6'	43° 5'	56°47'	79°29'	90°			
	221	26°34'	41°49'	53°24'	63°26'	72°39'	90°		
	310	8° 8'	58° 3'	45°	64°54'	73°34'			
	311	19°17'	47°36'	66° 8'	82°15'				
	320	7° 7'	29°45'	41°55'	60°15'	68° 9'	75°38'	82°53'	
	321	17° 1'	33°13'	53°18'	61°26'	70°13'	83° 8'	90°	
211	211	0°	33°33'	48°11'	60°	70°32'	80°24'		
	221	17°43'	35°16'	47° 7'	65°54'	74°12'	82°12'		
	310	25°21'	49°48'	58°55'	75° 2'	82°35'			
	311	19° 8'	42°24'	60°30'	75°45'	90°			
	320	25° 9'	37°37'	55°33'	63° 5'	83°30'			
	321	10°54'	29°12'	40°12'	49° 6'	56°56'			
		70°54'	77°24'	83°44'	90°				
221	221	0°	27°16'	38°57'	63°37'	83°37'	90°		
	310	32°31'	42°27'	58°12'	65° 4'	83°57'			
	311	25°14'	45°17'	59°50'	72°27'	84°14'			
	320	22°24'	42°18'	49°40'	68°18'	79°21'	84°42'		
	321	11°29'	27° 1'	36°42'	57°41'	63°33'	74°30'		
		79°44'	84°53'						
310	310	0°	25°51'	36°52'	53° 8'	72°33'	84°16'		
	311	17°33'	40°17'	55° 6'	67°35'	79° 1'	90°		
	320	15°15'	37°52'	52° 8'	74°45'	84°58'			
	321	21°37'	32°19'	40°29'	47°28'	53°44'	59°32'		
		65°	75°19'	85° 9'	90°				
311	311	0°	35° 6'	50°29'	62°58'	84°47'			
	320	23° 6'	41°11'	54°10'	65°17'	75°28'	85°12'		
	321	14°46'	36°19'	49°52'	61° 5'	71°12'	80°44'		
320	320	0°	22°37'	46°11'	62°31'	67°23'	72° 5'	90°	
	321	15°30'	27°11'	35°23'	48° 9'	53°37'	58°45'	63°36'	
		72°45'	77° 9'	85°45'	90°				
321	321	0°	21°47'	31°	38°13'	44°25'	50°	60°	
		64°37'	69° 4'	73°24'	81°47'	85°54'			

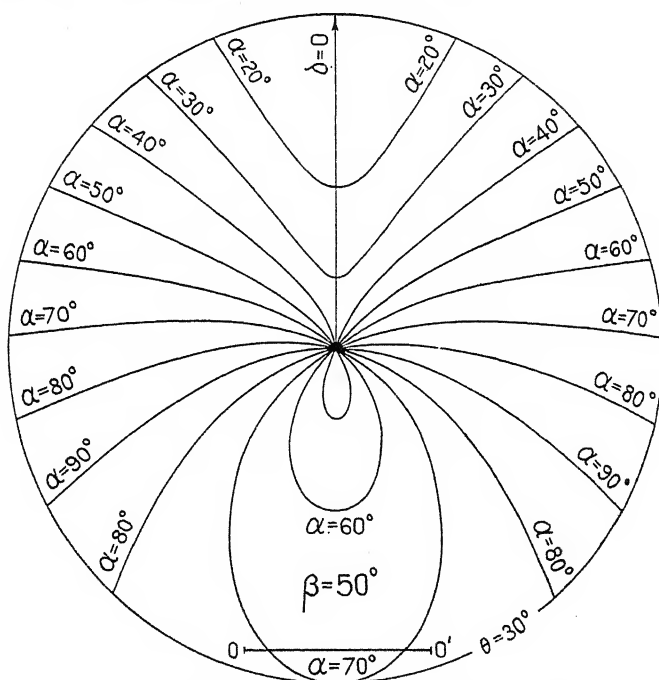
The pattern due to an electrolytic foil of nickel, reproduced in Fig. 5A, may serve to illustrate the method. For this photograph  $\beta$  was made 50°. The values of  $\alpha$  found from the chart are given in the second column of Table II; the values taken from Table I for  $(hkl) = (211)$  are given in the third column and this is the only value of  $(hkl)$  which gives even approximate agreement between columns 2 and 3. It will be noted that column 3 contains one value not found in column 2 but it is easy

to show that under the limitations imposed upon  $\beta$  and  $\theta$  the corresponding reflection cannot occur.

TABLE II

Reflecting planes $n(HKL)$	$\alpha(\text{obs.})$	$\alpha[\text{for } (hkl) = (211)]$
(111)	$61^\circ, 90^\circ$	$19^\circ 28', 61^\circ 52', 90^\circ$
2(100)	$36^\circ, 66^\circ$	$35^\circ 16', 65^\circ 54'$
2(110)	$30^\circ, 55^\circ, 73^\circ, 90^\circ$	$30^\circ, 54^\circ 44', 73^\circ 13', 90^\circ$

A second method of determining the plane  $(hkl)$  which coincides with the foil surface, was used in a few cases. This consisted in mounting the foil on a photographic spectrometer of the Bragg type, with the foil surface in place of the usual single crystal face. The foil was rotated with uniform angular velocity, and a screen containing an aperture, corresponding to the ionization chamber slit in the Bragg

Fig. 3. Chart showing lines of constant  $\alpha$  for  $\beta = 50^\circ$ .

spectrometer but  $10^\circ$  in width, was rotated with just twice this angular velocity. With this arrangement no planes can reflect x-rays on to the photographic plate except those lying very nearly in the plane of the foil. The photographs taken in this manner resemble closely those

taken with a single crystal. This method gave results confirming in every case those of the first method described. The second method, while it has certain advantages, is open to the objection that it does not permit a satisfactory estimate of the degree of special orientation, such as can readily be derived from the appearance of the diffraction patterns obtained in the first method.

### 3. EXPERIMENTAL RESULTS

Electrolytic films of Fe, Co, Ni, Cu, Zn, Ag and Cd, deposited under various conditions, were examined with x-rays in the ways described above. Table III gives a summary of the results obtained. All deposits, unless otherwise stated were made on copper at room temperature with a current density of 0.005 amp./cm<sup>2</sup>, and were 0.003 cm thick.

TABLE III.

<i>Metal</i>	<i>Solution</i>	<i>Special orientation</i>
Fe	FeSO <sub>4</sub> , 0.7m; NH <sub>4</sub> Cl, 0.8m; $P_h=5.0$ ; 50°C; current density 0.050 amp./cm <sup>2</sup> .....	(111) strong
Co	CoSO <sub>4</sub> , 1.0m; saturated with H <sub>3</sub> BO <sub>3</sub> .....	Not determined, medium weak
Ni	NiCl <sub>2</sub> , 0.1m; NiSO <sub>4</sub> 0.9m; H <sub>3</sub> BO <sub>3</sub> 0.6m; acid with H <sub>2</sub> SO <sub>4</sub> , $P_h$ varied from 3.5 to 6.1; 40°C.....	(100) strong
Ni	NiCl <sub>2</sub> , 0.9m; NiSO <sub>4</sub> 0.1m; H <sub>3</sub> BO <sub>3</sub> 0.6m; acid with H <sub>2</sub> SO <sub>4</sub> , $P_h=3.0$ .....	(211) strong
Ni	NiCl <sub>2</sub> , 1.0m; $P_h=4.0$ .....	None
Cu	CuSO <sub>4</sub> , 1.0m; H <sub>2</sub> SO <sub>4</sub> , 0.7m.....	None
Zn	Alkaline cyanide, Zn 0.5m, 40°C.....	None
Ag	Alkaline cyanide, Ag 0.2m.....	None
Cd	Alkaline cyanide, Cd 0.1m, 40°C.....	None

The effects of some of the different factors involved in deposition were investigated for the case of nickel. An interesting effect was observed when different thicknesses of this metal were plated from the same bath with the current density and other factors as nearly as possible the same, i. e., varying only the time of deposit. Photographs were taken using foils of thicknesses 2, 12, 23, 55 and 130  $\times 10^{-4}$  cm. The third and the last of these are reproduced in Figs. 5B and 5C, respectively. The photograph (not reproduced) taken with the thinnest foil shows no appreciable degree of special orientation. Fig. 5B shows that in the middle foil of the series the special orientation is appreciable, while Fig. 5C shows that in the thickest foil the crystals exhibit a decided tendency to become oriented so that their (100) planes are parallel to the surface of the foil. The photographs show, besides orientation effects, an increasing amount of x-radiation reflected on to the plate inside of the first Debye-Scherrer circle. This is general

radiation<sup>4</sup> of wave-lengths in the region 0.30 to 0.50Å, and its increasing prominence is due<sup>5</sup> to the fact that in increasing proportion the thicker foils are composed of very minute crystals, with dimensions of the order of 10Å. Fig. 5D shows the diffraction pattern obtained from the later-deposited half of the thickest foil, the first-deposited half having been etched away with nitric acid. This pattern compared with that for the entire foil (Fig. 7) shows weaker diffraction effects due to fine crystals, and shows a higher degree of special orientation than any of the other patterns.

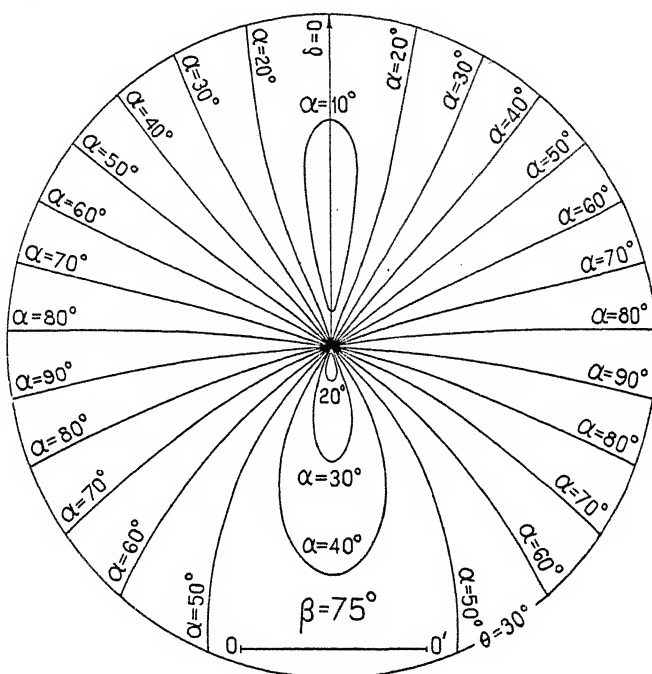


Fig. 4. Chart showing lines of constant  $\alpha$  for  $\beta = 75^\circ$

Some experiments were performed in which Fe, Ni and Cu were deposited in magnetic fields having various strengths and various directions with respect to the surface of the cathode. Other experiments were made using an inert (Pt) anode. Although these modifications seemed at first to change the degree or kind of crystal orientation in Ni, the effects were later traced to changes taking place in the solutions.

<sup>4</sup> R. M. Bozorth, J.O.S.A. and R.S.I. **9**, 123-127 (1924).

<sup>5</sup> Zsigmondy, Kolloidchemie, 3d ed. (1920), pp. 394, 403-5.

## 4. DISCUSSION OF THE RESULTS

The experiments described above show that some metals, when deposited electrolytically from solution, tend to form crystals oriented in a definite way with respect to the cathode surface. This tendency is greater in iron and nickel than in any of the other metals investigated. It is evident, however, in cobalt and silver. Preliminary experiments show that the degree and kind of special orientations are influenced to some extent by the composition of the solutions from which the metals are deposited.<sup>6</sup> Results already obtained support the belief that the special orientations are intimately connected with the state of stress which exists in the deposited metal. Kohlschütter and Vuilleumier<sup>7</sup> have shown that deposits of Fe, Ni and Ag, as usually produced, are in a state of tension, and experiments performed in this laboratory yield quantitatively the values of these tensions for different thicknesses of iron deposit. Also, Polanyi<sup>8</sup> has shown that the tension produced in metals by working produces special orientations of their crystals, and he has given an explanation for the production of such orientations. A natural explanation for the observed orientations in electrolytic foils is, then, that the tension known to be present in such foils produces orientations of the crystal grains in a way similar to that in which orientations are produced in hard drawn wires or rolled sheets. In this connection it is significant that the metals Fe and Ni, which are deposited in a state of tension and with special orientations of their crystals, are much harder mechanically than Cu, Zn and Cd in which the crystals are orientated approximately at random.

The cause of the tension which exists in the metals Fe, Co and Ni, and the manner in which this tension produces the crystal orientations, have yet to be considered. Experiments with Ni, however, indicate that a necessary factor in producing the tension is the hydrogen which is deposited along with the metal; in fact Kohlschütter and Vuilleumier<sup>7</sup> have shown that hydrogen electro deposited upon a thin nickel deposit produces in it a marked expansion, which disappears when the circuit is broken. On this basis the following mechanism is suggested for the production of the stresses in the deposits. The hydrogen which is deposited with each "layer" of metal causes the metal atoms to be laid down somewhat farther apart than they normally

<sup>6</sup> This is also the conclusion of R. Glocker and E. Kaupp from their work described in *Zeits. f. Phys.* **24**, 121-139 (May 22, 1924).

<sup>7</sup> V. Kohlschütter and E. Vuilleumier, *Zeit. f. Elektrochem.* **24**, 300-321 (1918).

<sup>8</sup> M. Polanyi, *Zeits f. Phys.* **17**, 42-53 (1923).

are in crystals of the pure metal. As successive layers are added, however, the forces which held the hydrogen in the deeper layers while they were being deposited, no longer exist, and the hydrogen diffuses out of the metal leaving it in a state of tension. Since this process

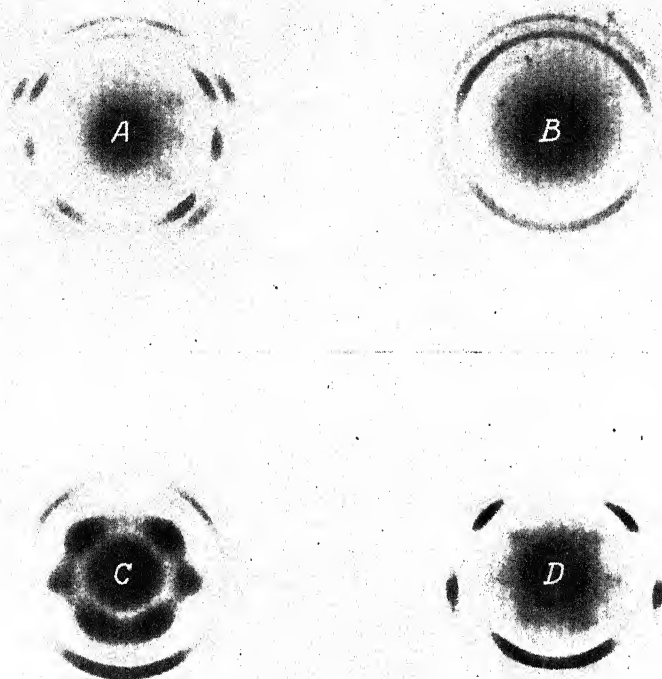


Fig. 5. X-ray photographs obtained with electrodeposited foils of nickel.

A.  $\beta = 50^\circ$ ,  $(hkl) = (211)$ .

B. Thickness  $23 \times 10^{-4}$  cm.

C. Thickness  $130 \times 10^{-4}$  cm.

D. Thick foil, later deposited half.

goes on continually during deposition the difference between the stresses in the innermost and outermost layers increases, and the compressive stress in the layer next to the cathode becomes greater and greater (but not, of course, in proportion to the thickness of the deposit.) The compressive stress in the layers first deposited may attain such a magnitude that some of the crystals are crushed, forming new crystals so fine that the reflection of x-rays by the metal is modified in a char-

acteristic way as seen in Fig. 5C and previously discussed. On the other hand, in the other layers where the crystals are formed under greater tension the orientations should be more marked, as was found to be the case.

It will be noted that the metals giving the most severely strained deposits are those of the iron group. Silver, which follows these in the intensity of strains and degree of special orientation is the next element following palladium. McKeehan has shown<sup>9</sup> that the space-lattice of palladium is expanded when it is made the cathode of an electrolytic cell producing hydrogen, and that the lattice again contracts upon the loss of hydrogen. The effects here discussed emphasize again the often-noted anomalies, magnetic and otherwise, associated with the eighth group elements and their neighbors in the periodic table.

In conclusion I wish to acknowledge my indebtedness to Dr. L. W. McKeehan and Dr. R. M. Burns for helpful discussions concerning the structure of electrodeposits, and to Mr. C. W. Warner for preparing some of the foils.

BELL TELEPHONE LABORATORIES, INCORPORATED,  
NEW YORK, N.Y.,  
June 1, 1925.

<sup>9</sup> L. W. McKeehan. *Phys. Rev.* (2) 21. 334-342 (1923).



## BINAURAL BEATS

By C. E. LANE

## ABSTRACT

By introducing a tone of frequency  $f$  into one ear and another tone of frequency  $f+N$  into the opposite ear, where  $N$  is less than 5 or 6 cycles, two kinds of binaural beats are obtained. *Objective binaural beats* are heard for most values of  $f$  within the audible frequency range, provided there is the proper difference in amplitude between the two tones. For telephone receivers as sound sources, this difference for best beats is about 55 TU and for the same receivers supplied with sponge-rubber cushions about 62 TU. These beats are heard because the louder tone is conducted through the head to the ear of the weaker tone and the two tones there are about equally loud. *Subjective binaural beats* are heard for frequencies below 800 or 1000 cycles when the tones at the two ears have about the same amplitudes, differing by not more than 25 TU. Data obtained with 22 observers are summarized. The evidence indicates that these beats are not due to cross conduction but are of central origin and the result of the sense of binaural localization of sound by phase. If the beats are slow (less than 1 per sec.) they are generally recognized as an alternate right and left localization, though some observers may report one or more intensity maxima during the beat cycle. Such maxima are explained as the result of one's interpreting the sound as louder when localization is more definite. Fast beats (more than 1 per sec.) are generally recognized as an intensity fluctuation. They are explained by assuming that the sound appears louder when the phase relations are such that it is normally best localized in the position toward which the attention is directed. This explanation is supported by observations made with a constant source rotating around the head of a listener.

## INTRODUCTION

THIS paper is concerned with experiments undertaken to determine the nature of "binaural beats." Binaural beats of one kind have been described by G. W. Stewart<sup>1</sup> and others. Binaural beats of another kind were observed by R. L. Wegel and the writer<sup>2</sup> in making measurements of binaural masking. That the nature of these two kinds of beats was different was not appreciated until the investigation reported here was begun. In the work of Wegel and Lane the beats were investigated only sufficiently to show that their existence did not invalidate any conclusions proposed concerning the mechanism of hearing.

<sup>1</sup> G. W. Stewart, Phys. Rev. 9, pp. 502, 509, 514 (June 1917).

<sup>2</sup> R. L. Wegel and C. E. Lane, Phys. Rev. 23, (March 1924).

We shall use the "transmission unit"<sup>3</sup> recently adopted by the Bell Telephone System. Taking for each frequency the threshold value as the unit of a geometrical scale, the magnitude of any tone in transmission units is numerically equal to ten times the common logarithm of the ratio of the intensity of the tone in the ear canal to the threshold intensity. If a tone is of such an intensity that the rate at which sound energy enters the ear is ten times that required for minimum audibility the magnitude of the tone is said to be 10 TU, if 100 times 20 TU, etc.

As an illustration of the phenomenon of binaural beats, it may be stated that if, by means of telephone receivers, two tones of 250 and 251 cycles are introduced into opposite ears, and if the intensity of the first or primary tone is kept constant at 80 TU above threshold while the intensity of the other or secondary tone is gradually increased, starting at zero, the sensations produced are as follows: Nothing but the steady primary tone is heard until the secondary reaches a value of 5 or 10 TU when very faint beats or intensity fluctuations become perceptible. These beats gradually become more intense until at about 25 or 30 TU they are loudest. For a further increase in the intensity of the secondary tone the beats gradually become fainter and at about 45 or 50 TU disappear. When the intensity of the secondary tone is increased to 60 TU, beats again are heard. However, these beats differ in many ways from those first observed. When the intensity of the secondary tone reaches about 80 TU, or when the two tones are equally loud, these new beats are heard best. They disappear when the intensity of the secondary tone reaches about 100 TU.

The nature of the beats and the range of relative intensities for best beats depend somewhat upon the frequency of the beating tones, the frequency of the beat, and the manner in which the sounds are introduced into the ears. The beats that are heard best when the tones are greatly different in intensity are designated objective beats and those that are heard best when the tones are equally loud, subjective beats. The reason for this terminology will appear later.

<sup>3</sup> The difference  $S$  in TU (transmission units) between two tones of the same frequency is defined by  $S = 10 \log_{10} (I_1/I_2)$  where  $I_1$  and  $I_2$  are their respective intensities. See the following papers:

- H. Fletcher, *Jour. Franklin Inst.* (Sept. 1923).
- H. Fletcher, *Phys. Rev.* **23**, 427 (March 1924).
- Martin and Fletcher, *Jour. A. I. E. E.* (March 1924).
- W. H. Martin, *Bell Tech. Jour.* (July 1924).
- Fletcher and Steinberg, *Phys. Rev.* **24**, 306 (Sept. 1924).
- R. V. L. Hartley, *The Electrician* (Jan. 16 and 23, 1925).

## APPARATUS AND METHOD

The apparatus was essentially the same as previously used in this laboratory in the determination of the frequency sensitivity of normal ears<sup>4</sup> and the auditory masking of one tone by another.<sup>2</sup> Telephone receivers were used as sound sources. The currents at different frequencies were supplied by means of vacuum tube oscillators equipped with filters to eliminate effects due to harmonics. Two voltage attenuators were used, one associated with each receiver. In taking the data on objective beats, minimum audibility was separately determined for each receiver on the same ear. The primary tone was then adjusted to 80 TU above minimum audibility and the receiver transferred to the opposite ear. Then with the receiver supplying the secondary tone on the first ear, its output was adjusted until best beats were heard.

For taking the data on subjective beats, minimum audibility was again determined for each receiver on the same ear. The tone from both receivers was then adjusted to the same level above minimum audibility and one tone presented to each ear. In order to determine the phase relation at any time between the tones from the two receivers, an auxiliary receiver was connected through an amplifier across the input of the two attenuators. By listening to this receiver, a second observer could at any time report the phase relations.

## OBJECTIVE BEATS

1. *The relative intensities of the two tones for hearing objective beats.* The difference in TU between tones for best hearing objective beats was obtained first without and then with rubber cushions between the ear and the receiver cap. The observed values are given in Table I. A deviation of 20 or 25 TU on either side of the values given usually resulted in the disappearance of the beats. The table presents data for two different observers, both of normal hearing. The frequencies of the primary tones used are given in the first column. In taking the data the secondary tone differed from the primary by about one cycle. Three successive determinations of the difference between the two tones for best beats were made for each frequency. The averages of the values thus obtained are shown. The agreement between the two observers is very satisfactory. It is seen that the addition of rubber cushions has increased the intensity difference for hearing best beats about 7.0 TU.

2. *Theory of objective beats.* In monaural hearing where the two tones are introduced into the same ear, beats are heard best when the magnitudes of the two tones are equal, and beats cannot be heard at all if

<sup>4</sup> Fletcher and Wegel, Phys. Rev. 19, 553 (June 1922).

the tones differ by more than about 30 TU. The data below give as the average difference for best hearing the objective binaural beats, a value of about 55 TU when using receivers without cushions and 62 TU with the cushions. In consideration of these facts, there seems to be only one possible explanation for the hearing of objective binaural beats. The beats evidently originate in the ear of the weaker tone, the louder tone being conducted across the head to this ear where interference takes place. When the magnitudes of the two tones are adjusted for best beats their difference corresponds approximately to the difference in sound energy of the louder tone at the two ears.

TABLE I  
*Difference between tones for best beats*

<i>f</i>	Without cushions		With cushions	
	(C.E.L.)	(A.G.)	(C.E.L.)	(A.G.)
200	54 TU	48 TU	67 TU	54 TU
300	61	44	68	55
400	57	64	64	66
600	49	61	66	70
1000	47	50	49	57
1500	42	49	47	59
2000	50	57	52	61
3000	63	62	67	62
4000	69	69	75	72
Average	54.7	55.5	61.7	61.4

Measurements of the difference between the response of an ear to a tone introduced into it by means of a telephone receiver and the response of this ear to the same tone when introduced into the opposite ear have been determined by two other independent methods. The data were taken for the same range of frequencies as shown in Table I. In the first method it was found for a person entirely deaf in one ear that the average difference in intensity required for minimum audibility between a tone in the good ear and in the bad ear was about 58 TU. In the second method it was found that for a loud tone of one frequency to just mask a faint tone of another frequency the loud tone must on the average be about 56 TU louder when presented to the ear opposite the faint tone than when presented to the same ear.<sup>2</sup> These values agree well with the values of 55.5 TU and 54.7 TU as determined by the beat method.

3. *Sound conduction from one ear to the other.* There are four ways in which a tone introduced into one ear may get across to the opposite ear.<sup>5</sup> First, it may pass around the head through the air. Second, if

<sup>5</sup> It is assumed that the receivers at each ear are not joined mechanically as by a head band.

the sound source is held against the ear, the vibrations in it may be communicated directly to the flesh and bones of the head and thence across. Third, the varying air pressure at the ear causes the bones of the inner ear and the other surrounding bones to vibrate even though the sound source may not be directly in contact with the head. In this way sound likewise reaches the remote ear by bone conduction. Fourth, the motion of the ear drum of the proximal ear may transmit air waves through the Eustachian tubes to the opposite ear.

If the sound source is not held against the ear, in most cases the greatest part of the sound reaching the opposite ear arrives there by air-conduction around the head. If the sound source is held against the ear as in the case of telephone receivers, most of the sound reaching the remote ear arrives there by bone-conduction and is the result of direct communication to the head of vibrations in the receiver cap. This conclusion was reached after trying the following experiment. The external meatus of the ear into which the louder tone is introduced was plugged and the receiver on the other ear covered by heavy layers of sound absorbent material. The relative intensities of the two tones for best beats was found to be the same as before. No satisfactory way has yet been found for determining the effectiveness of the other two paths in conducting sound across the head.

Since the purpose of this investigation was to explain the beats rather than to make an exact determination of the difference between the primary and secondary tones for best beats for an average observer using average receivers, no large amount of data was taken. However, the data obtained show that, while the difference for best beats as determined for some one primary frequency may vary as much as 10 or 15 TU for the same observer using different receivers or for different observers using the same receivers, the averages of the differences as determined for a range of frequencies between 200 and 4000 cycles is nearly independent of both observers and receivers, provided the receivers are not radically different. The irregular variation of the data with frequency is primarily the result of the complex path by which the primary tone reaches the remote ear, and the variations for the same frequency for different observers or different receivers are the result of small changes in the various elements constituting this path.

4. *Localization of objective beats.* In connection with the hearing of objective beats it was observed that the beats are generally localized in the ear of the louder tone. This, however, is not an argument against the explanation already given which states that they are actually due

to interference in the other ear. Localization of the varying stimulus is one thing and the recognition of its existence is another. The remarkable independence of the two ears enables one to hear weak beats in one ear in the presence of a very loud tone in the other, but this loud tone so holds the attention that one locates the beats as coming from the latter ear. It should be added that localization of the beats in the ear of the louder tone does not always occur. Two observers who first localized them in this ear, later, after a little practice, best localized them either in the other ear or somewhere between the ears.

A phenomenon similar to this has been observed in listening to two tones quite different in frequency. If one of these tones is presented to one ear it is localized in that ear, but if a much louder tone of another frequency is at the same time presented to the opposite ear the localization of the first tone may be shifted somewhat though the tone still remains distinctly audible.

#### SUBJECTIVE BEATS

1. *The effect of varying the beat frequency of subjective beats.* As stated above subjective beats are those heard best when the tones are equally loud. Data for the determination of the effect of varying the beat frequency of these beats were taken for 22 observers. Most of the observers had no preconceived notion as to what they were going to hear and care was taken to offer no suggestions that would influence them in the interpretation of their sensations. The frequencies used were 250 and  $250+N$  cycles where  $N$  was the beat frequency.  $N$  was varied for most of the observers from  $1/4$  to 4 cycles. For the sake of simplicity in recording the data, the higher frequency was always presented to the right ear. Receivers supplied with the sponge-rubber cushions were used. However, preliminary tests showed that the character of subjective beats heard was unaltered by the use of receivers without cushions or by the presentation of the tones to the ears through rubber tubes.

We will first consider the experiences of the 22 observers while listening to slow beats, meaning by slow beats those having periods of more than one second. Four of them reported hearing nothing but a steady tone of rather indefinite localization somewhere within the head. The other 18 recognized the beat period by an alternate right and left localization, the sound being best localized on the side of the tone leading in phase. Their experiences, however, during the time of transitions of localization from one side of the head to the other differed.



Three of them reported no sense of motion but simply an alternate rising and falling of intensities at the two ears, the sound being equally loud at the two ears at the time of agreement and opposition of phase. Seven described the localization as passing along a path either just outside or inside the front or top part of the head during phase agreement and through the lower or back part during opposition, the latter path being less definite than the former. One observer at one time reported the sound as passing back of the head during agreement in phase and at another time in front. In both cases the sound passed straight through the head from one ear to the other during opposition in phase. Two observers reported the sound as passing from left to right and right to left along the same path. For one, this path was through the back of the head and for the other directly between the ears. One described the sound as traveling in a horizontal circle outside the head and at a distance, passing in front during phase agreement and in back during opposition. Another reported the sound as traveling in a circle outside the head. However, in this case the circle lay entirely back of the head. One observer reported the localization as passing through the back of the head at the time of opposition of phase and a period of no localization during phase agreement. Still another reported definite localization in front part of the head during agreement in phase and no localization during opposition. The last of the observers experienced a sensation of motion but was not able to assign any definite path to it.

The reports of the observers as to intensity maxima for the slow beats were as follows. Four reported no maxima. Three reported a maximum at the time of phase agreement located in the front part of the head. One at first reported a maximum at the time of phase agreement but later reported it just before opposition in phase and located in the right ear. Three observers reported a maximum in the right ear just before opposition in phase. Six reported two maxima, one in each ear shortly before and shortly after opposition in phase. The other observer most of the time reported a maximum at each ear but on two occasions reported a primary maximum in the top of the head at the time of phase agreement in addition to the two secondary at each ear.

All but four of the observers who listened to the slow beats listened to beats of intermediate and fast frequencies. Intermediate refers to beats from one to two times per second and fast to beats occurring more than twice per second. Of the 18, four were not able to report the beta frequency for the intermediate beats. Six described an intensity fluctuation inside the head of rather indefinite localization accompanied by a



rather vague sense of motion. Four described an intensity fluctuation within the head of the same frequency of the beat accompanied by a sensation of sound localization describing a circle above the head but with only half the beat frequency. Three reported the sound localization as describing a circle above the head corresponding to the beat frequency. The last described the sound as shooting through the head from left to right at the time of phase agreement.

As to the existence of intensity maxima for intermediate beats, only about half of the observers were able to satisfactorily report the time at which such maxima occurred. Most of these reported the maxima as occurring either at  $0^\circ$  phase difference or at about  $120^\circ$  phase difference. Some changed from one of these phase relations to the other during the course of the experiment.

All of the observers who listened to fast beats could notice an intensity fluctuation but two or three were not able at any time to report the beat frequency. Some could report the beat frequency only part of the time. Only one of the observers reported any sensation of motion.

It should be added here that the experiences of all the observers while listening to subjective beats were very indefinite and difficult for them to describe. Their reports were in some cases more inconsistent than the preceding data might indicate. Several observers at times spoke of periodic changes in quality that assisted in the recognition of the beat, but were not able to define the nature of the change. The data as given are in agreement with the observers' most consistent reports of their experiences.

2. *Effect of varying the frequency of the beating tones.* Data were also taken to determine the effect of increasing the frequency of the tones producing subjective beats. Seven observers who could follow the beats at 250 cycles with the least difficulty were used. The beat frequency was kept constant at one beat per second. All were able to hear the beats for frequencies as high as 600 cycles, only two as high as 800, and only one as high as 1,000. For frequencies higher than 1,000 cycles none were able to hear the beats.

3. *The range of relative amplitude for hearing subjective beats.* Data were taken for a few observers to determine the range of relative intensities over which subjective beats are audible. The limiting difference between the two tones for hearing the beats was found to be somewhere between 20 and 25 TU. Thus the breadth of the range of relative intensities for hearing subjective beats is about the same as it is for objective binaural beats. Therefore, when the attenuation of sound

in passing through the head is greater than 40 or 50 TU there should in general be a range of relative intensities between the ranges for hearing objective beats and subjective beats for which no beats are audible. Such is found to be the case.

4. *Summary of essential facts.* The following are the essential facts revealed by the data on subjective beats:

(a) If two tones of equal intensities and nearly the same frequencies are simultaneously presented to opposite ears, the beat frequency can be recognized by about 80 percent of the observers provided the frequencies of the beating tones are less than 800 or 1000 cycles. For higher frequencies the beats cannot be heard.

(b) If the beats are slow, the one outstanding phenomena observed by all who recognized the beat is an alternate left and right localization of the sound, localization being on the side of the tone leading in phase.

(c) Most observers who hear the slow beats experience a more or less vague notion of the localization traveling along some path through the median plane when the localization shifts from one side of the head to the other, but there is no good agreement among the observers as to the position of this path.

(d) The passing of the localization through the median plane is generally more clearly defined during phase agreement than during phase opposition.

(e) While all observers who heard the slow beats, reported without any previous suggestions the existence of the alternate right and left localization, none reported any intensity maxima until questioned as to the existence of such maxima. However, when questioned, over 80 percent of the observers reported maxima corresponding to one or more of the following three phase relations: (1) phase agreement, (2)  $30^\circ$  or  $40^\circ$  before opposition and (3)  $30^\circ$  or  $40^\circ$  after opposition. There was no good agreement among the observers and several during the course of the experiments shifted from one phase relation to another in their report on the time of intensity maxima.

(f) For fast beats the chief sensation is that of an intensity fluctuation of the sound located somewhere within the head.

(g) For intermediate beats some reported a predominating sensation of motion, others of intensity fluctuation and still others seemed to experience both sensations about equally well and could direct their attention upon either at the sacrifice of the other.

(h) Subjective beats are heard equally well for tones introduced into the ears by means of telephone receivers with and without receiver cushions or presented by means of rubber tubes.

(i) So long as the two tones are of equal intensity, the hearing of subjective beats is independent of their loudness.

6. *Theory of subjective beats.* Most writers on the subject of binaural localization of sound agree that such localization for low frequencies is the result of direct perception of the phase difference at the ears. This means that the vibratory character of the sound does not terminate at the end organ but is in some form transmitted to the brain. This sense is not highly developed and generally exists only for frequencies below 700 or 800 cycles. The theory advanced here for subjective beats attributes the hearing both of the right and left effects observed and of all intensity maxima to the sense of binaural localization and, therefore, places the origin of these beats in the brain.

Stewart has offered a very complete cross-conduction theory for explaining the binaural beats here called subjective, but at the same time has recognized that many good arguments may be advanced against such a theory. In consideration of the facts presented on the preceding pages there are several reasons why some theory not based on peripheral interference should be used for explaining these beats. First, the attenuation of the sound in passing through the head is far too great to permit perceptible amplitude fluctuations at the ears when the tones there are equally loud. Data on monaural hearing show that one cannot detect variations at the ear that are less than .5 TU whereas a cross-conduction theory requires the perception of variations of the magnitude of .03 TU to .003 TU or even less. Second, if cross-conduction were responsible for the hearing of these beats, their clearness should, in some way, depend upon the amount of cross-conduction. The use of different sound sources for which there are known differences in the amount of cross-conduction shows that such is not the case. Third, if the subjective beats were due to cross-conduction, the hearing of them should not be limited to frequencies for which binaural localization by phase is possible. Fourth, there is a range of amplitude ratios for which beats cannot be heard which is between the range for hearing the subjective beats and the range for hearing the objective beats. If the beats were all caused by cross-conduction, they could be heard over the entire range.

There are many reasons for believing that binaural subjective beats are the result of binaural localization by phase. These beats can only

be heard for frequencies that can be localized by phase. When the beats are slow, the chief phenomenon observed is that of wandering localization. When intensity maxima are indicated, they are associated with positions of best localization, as localization in the median plane or at the two ears. It is not surprising that the sound should be considered louder by most observers at the time of best localization for the mind can best attend it then. The sound is generally localized in the median plane at the time of phase agreement, but the localization in this plane is different for different observers. This is as it should be, for the position of a sound cannot be localized in the median plane by phase alone. The uncertainty of localization and lack of agreement among observers for phase differences in the neighborhood of  $180^\circ$  are likewise to be expected. Observers are then listening to phase relations with which they have never learned to associate positions.<sup>6</sup> The experiences reported, therefore, depend upon the psychological reaction of the observers to an entirely new phenomenon.

When the beat frequencies are fast the nature of the mind makes it impossible to follow the sound in any wandering path of localization. The attention would have to move from one position to another entirely too fast. As a result the attention is centered on some definite localization and the sound appears louder when the phase relations are such that the sound is best localized in this position. The beats then are not intensity fluctuations in the ordinary sense, but rather rapidly recurring conditions for definite localization.

At intermediate beat frequencies one may be able to recognize that the localization of the sound is wandering when the frequency is too fast to follow in its path of localization. This accounts for the fact that the correct frequency of the beats is not given if one reports it from the apparent period of wandering localization. However, if attention is only directed upon apparent intensity fluctuations for one position of localization, beats of the correct frequencies are heard for the same reason as that given for hearing the fast beats.

Additional plausibility is given to the explanation offered above for subjective beats by the results of the following experiment: A receiver emitting a pure tone was caused to describe a circle in a horizontal plane about the head of an observer in a large room with non-reflecting walls. When the receiver moved slowly it was observed to pass from left to right and back again with little or no intensity variation of the tone.

<sup>6</sup> R. V. L. Hartley and T. C. Fry, *Phys. Rev.* **18**, 431 (Dec. 1921).

However, when the receiver made three or more revolutions per second one was not aware of any motion of the sound source but an apparent intensity fluctuation corresponding in frequency to the number of revolutions was observed.

BELL TELEPHONE LABORATORIES, INCORPORATED,  
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## BOOK REVIEWS

**The New Theories of Matter and the Atom.** ALFRED BERTHOUD. Translated from the French by Eden and Cedar Paul.—The great advances which have been made in recent years in the field covered by this book have fascinated the scientific mind and created a desire among intelligent men to acquire some understanding of the new developments. This desire is properly being met by the appearance of a considerable number of books on the subject written in a non-technical style. The work under review is a somewhat more advanced type of this kind of book. The ideas which have prevailed regarding the nature of matter are developed for the most part in chronological order, and a very good account is given of the current theories. Its style makes the book very readable. In a field where there is at present so much speculation it is difficult to present matters so that the reader will always clearly understand the extent to which the different ideas are generally held. The author, for example, accepts the numerical equivalence of mass and energy and uses it in a number of calculations throughout the book without pointing out that this equivalence is held to be more speculative than other portions presented. Michelson alone is given the credit for the Michelson-Morley experiment. The misspelling of Michelson's name throughout the book is unfortunate. Ramsay and Soddy, instead of Rutherford and Soddy, are credited with the theory of atomic disintegration. It is stated that incandescent substances give off electrons when exposed either to x-rays or to ultraviolet light, whereas these agents are not necessary. It is a sign of the rapid progress in science that, contrary to statements made in this book, there is no longer a hiatus between infrared and Hertzian waves, and x-rays are now known to be refrangible. The French term milliard is used throughout, although in America, at least, we have an English equivalent. The book is to be highly recommended to those desiring an authentic account of this all-important subject. Pp. 259. The Macmillan Company, New York, 1924. \$3.50. JOHN ZELENY

**Foundations of the Universe.** M. LUCKIESH.—This book is one of a series of volumes issued under the title of *Library of Modern Sciences*. It appears to be the object of this series to give the present state of knowledge in various fields in language that is not technical and in a form to make the reading interesting to the general reader. The author of the volume under review starts out with the statement that knowledge of the physical world has been the foundation of civilization and he emphasizes throughout man's relation to the physical universe and his limitations in attempting to understand it fully. The whole treatment is along very broad lines. There is no attempt at a systematic treatment and yet there is system in it. A chapter on men, atoms, and stars is followed by chapters on matter and motion, and on molecular motion. Then follow chapters on the nature of light, what is space, the velocity of light, and the epoch of Einstein. These are followed by portions on the elements of matter, the electron theory, and the evolution of the elements. Next we come to, inside the atom, the quantum of energy and atomic structure. The treatment proper closes with a philosophical chapter on the fateful unknown, at the end of which are some speculations on the existence of an omnipresent Mind that is at the bottom of things. A chapter on the growth of knowledge gives an interesting list of great names in the physical sciences arranged chronologically and stating in a few words what each chiefly contributed. A final chapter gives a table of

important units and magnitudes. As is seen from the contents, the author has stressed those parts of physics which have been receiving most attention in recent years and these parts comprise the foundations of the Science. The general reader must not expect to acquire a deep comprehension of the field treated by reading a popular book like this but he will at least have had a vision showing him what it is all about, and will have found food for much thought.—Pp. viii+245. D. Van Nostrand Company, New York. 1925. \$3.00.

JOHN ZELENY

**Die Grundlage der Macschen Philosophie.** HUGO DINGLER.—In this little book of 106 pages the author gives at first with greatest sympathy and admiration, a short biography of Mach. He then proceeds to Mach's general attitude toward the problems of physics, philosophy, and physiology. Mach himself rejects the title of a philosopher; he considers himself merely as a philosophic dilettant (*philosophischer Spaziergänger*). Grown up in close and sympathetic contact with nature, Mach was a collecting scientist, a quiet and unassuming investigator, who tried to go to the bottom of things. Kant's problem of knowledge or epistemology had a decisive influence on Mach's thinking; nevertheless, Mach tried to eliminate all metaphysical elements from physics and especially the "thing in itself." This tendency led Mach to reject the atomic theories in physics and chemistry and, finally, the theory of relativity, even though some of his criticisms of Newton's dynamics led half a century later to that general theory. Mach calls the last principles of science instinctive, and his instinctive knowledge is not very different from Kant's a priori knowledge.

Mach wanted to arrive at a theory of knowledge on the basis of physical sciences by an inductive method; he considered physics as a natural object, as a historic-biological process in the life of the species "homo sapiens." The world with his own self appeared to Mach as one continuous mass of sensations, only stronger connected in the "I." In order to master the multitude of sensations by thinking, Mach considers the principles of "economy" and of adaptation "of thoughts among themselves and to the facts"; so he is driven toward sensualism and empiricism, still avoiding any dogmatic system and continually asking the deeper questions of the validity of the underlying principles of the physical sciences, a problem of philosophy which he is unable to solve.

Dingler devotes a special chapter to Mach's relation to relativity. Mach considered all motions as relative, even the rotations; he rejected absolute space and time. Rotations are relative with respect to the stars. This thought plays an important rôle in the general theory of relativity by A. Einstein, a theory which Mach decidedly refused to accept.

Mach's principal work is probably *Die Mechanik in ihrer Entwicklung*. This classical work forms largely the basis of Dingler's discussion. I should have liked to see a deeper study of Mach's *Die Analyse der Empfindungen*. Even without this analysis I wish to recommend this beautiful little book of Dingler's to the physicists.—Pp. 106. Johann A. Barth, Leipzig, 1924.

JAKOB KUNZ

**Die Theorien der Radiologie.** Marx Handbuch der Radiologie, Vol. 6.—This final volume of the series is devoted largely to theories of electrons and quanta. Chapters on theory of motions of electrons and of passage of alpha and beta particles through matter and a note on the Compton effect are contributed by von Laue. Chapters on the Zeeman effect, experiment and theory, are by Zeeman and Lorentz. A brief statement is given by Sommerfeld and Wentzel of the principles of quantization and their extension to non-hydrogenic atoms. Experiments on excitation of atoms by radiation and by electronic and atomic collisions and the theoretical bearing of the work are compactly presented by Joos. A long chapter by Riecke on electron theories of metals, written in 1913, is supplemented by von Laue. Vegard gives a detailed account of observations and theories of the "Northern Lights." Debye contributes a thorough presentation of theories of electric and magnetic molecular properties.



The names of the contributors vouch for the quality of the papers. In a compilation of this type some overlapping and many omissions are unavoidable. Generally speaking, the omissions (notably in various phases of the quantum theory) are adequately covered in other recently published books, while less accessible material has been given well merited prominence.—Pp. 806. Akademische Verlagsgesellschaft m.b. H. Leipzig, 1924, Price, \$10.00 bound; \$9.60 unbound.

F. L. MOHLER

**Grundbegriffe der Mechanischen Technologie der Metalle.** GEORGE SACHS.—This book, which is volume II of a series entitled *Der Metallische Werkstoff, Gewinnung, Behandlung, Veredlung* and edited by W. Guertler, is addressed to the reader with physical training but with no acquaintance with technical operations. It endeavors to present a summary of all the fundamental experimental facts and of the established theory of those mechanical properties of metals which are involved in ordinary engineering and manufacturing operations. A knowledge of a certain amount of the material of this book should be in the possession of every liberally educated physicist, for the behavior of many kinds of physical instrument is affected by such phenomena as elastic hysteresis, for instance. The physicist whose interests take him closer to technology will find this a most valuable summary of a very wide and complicated field, in which there has been much recent progress, and which is nowhere collected into accessible form.

The book is mostly concerned with the behavior of pure metals outside the range in which Hooke's law holds, that is, in the range of permanent set or flow or elastic after-effects, which is really the actual range of all the metals of practice. In the first hundred pages the behavior of metals is described disregarding their small scale crystal structure including the usual subject matter of the testing laboratory, such as tensile, compression and torsion tests, with a discussion of the various hardening effects of over-strain. There follows a longer discussion of the part played by crystal structure in deformation and hardening. This proceeds from an interesting discussion of the recent work of Polany and his collaborators on the deformational properties of single metal crystals, which will be of interest to the pure physicist quite apart from the more technical applications, to a discussion of all the complicated properties of metals which involve their structure as crystalline aggregates. The range of facts covered in this discussion is very wide! The comparatively small space devoted to a discussion of the various theories of the phenomena indicates how far this field is from being a closed one. At the end is a summary in about fifty pages of the mechanical properties of alloys, which will be convenient for those who do not care to consult the more elaborate works. There is also a long bibliography, probably as complete as could be expected in a work of this character, which will be useful to many. The convenience of the book for reference purposes is much increased by a very complete index.—Pp. xii+319, 23×15 cm, with 29 tables and 232 diagrams. Akademische Verlagsgesellschaft M.B.H., Leipzig. 1925. Unbound \$3.15, bound in cloth \$3.60.

P. W. BRIDGMAN

**Physikalisches Handwörterbuch.** ARNOLD BERLINER and K. SCHEEL.—It is said to be impossible to indict a whole nation, and it must be equally so to review a whole dictionary. However, here are some facts about this dictionary; it is over 900 pages long, well printed in double columns on good paper and well bound. The pages are  $7\frac{1}{2}'' \times 10\frac{1}{2}''$ . The articles range in length from a sentence to several pages, and cover not only the field of physics, but large areas of chemistry, astronomy, geophysics, meteorology, even of geology. The list of authors extends to fifty-nine and includes such impressive names as Freundlich, Gerlach, Grebe, Gumlich, Marx, Pauli, von Rohr, and Westphal. The articles and cross-references are arranged in a single alphabetical series, as in a regular dictionary, not in a series of articles with an index to provide the cross-references, as in an encyclopædia.

As for the quality of the articles, they are much better than I should have thought possible. It does not seem promising to find the information about the contemporary atom-model distributed under the scattered headings *Bohrsches Korrespondenzprinzip*, *Bohr-Rutherford'sches Atom*, *Quantenzahlen*, *Quantentheorie*, *Adiabatenhypothese*, *Zeemaneffekt*, *Störungstheorie*, and I do not know how many others; but this system has the great advantage that one can understand the account of a subject printed, say, on page 500, without being forced to read all through from page 1 to page 499 as a preliminary. Some of the authors have not hesitated to give condensed synopses of such subjects as canonical equations, theory of perturbations, metallic reflection, and equations of impact. The articles on the various aspects of atomic theory seem to represent the state of knowledge "as of" about 1922; the book is dated 1924, but the difference between these dates is easy to justify, and is explained in the unusually candid preface. The most inadequate article I have noticed is that on photo-electricity (masked as *Hallwachseffekt*) which might have been written in 1912. Curiously enough, there is no article headed *Elektron*—only a poor cross-reference appears under this head—but *Subelektron* has a paragraph.<sup>2</sup> However, I do not wish to end on a note of dispraise. The dictionary is distinctly recommendable for libraries, although the individual physicist may well hesitate to pay the price (which, however, seems not exorbitant as prices go).—Pp. vi+903. Julius Springer, Berlin. 1924. Price \$9.30.

KARL K. DARROW

**College Physics.** A. WILMER DUFF.—This book is intended as a textbook for a beginning course, of which demonstration lectures form a part. The book is therefore concise, and does not contain a great deal of purely illustrative material or technical applications. The topics treated in the book are clearly presented and the phenomena described are intimately connected with the principles to be illustrated.

Reversing the usual order, statics is presented before dynamics. Unity in the treatment of the subject matter is sought by using energy as the fundamental idea throughout. To this end the introduction of the ideas of work and energy is made in the very beginning, and they are used in the subject of statics, as well as in the later topics. A novel frontispiece emphasizes the important rôle of energy as the fundamental thing in physics. It presents "A Brief History of Physics" in the form of a branching tree and should prove instructive.

Many teachers will feel the lack of a discussion on the subject of dimensions. The substitution of the names "Harmonic Vibration" and "Harmonic Oscillation" for Simple Harmonic Motion and Angular Simple Harmonic Motion seems rather unfortunate as long as the latter terms are used almost universally in the literature of physics.

There are discussions, in the appropriate places in the book, of some of the results of modern research. These discussions are not intended to give the student a working knowledge of the topics treated, but they do serve to give him some idea of the trend in modern physics. References are given for more extended reading. Among the modern topics treated are, Relativity, Electron Theory, Atomic Structure, Quantum Theory, Bohr's Theory of Spectra, and Crystal Structure. Many teachers will wish for a more complete incorporation of the electron theory into the treatment of electricity.

Among the features which should prove of value to students are the "Suggestions to Students" in the beginning of the book, the lists of suggestive questions and the numerical problems at the end of the chapters, and the many worked-out problems. In an appendix are given calculus derivations of some important formulas. This book should prove a valuable addition to the available textbooks.—Pp. xii+484, 499 figures, 27 tables. Longmans, Green and Co.; New York. 1925. Price \$3.80.

J. R. COLLINS

**Physics for Technical Students.** WILLIAM BALLANTYNE ANDERSON.—Second edition, revised and enlarged.—From the preface, this edition contains 50 new figures

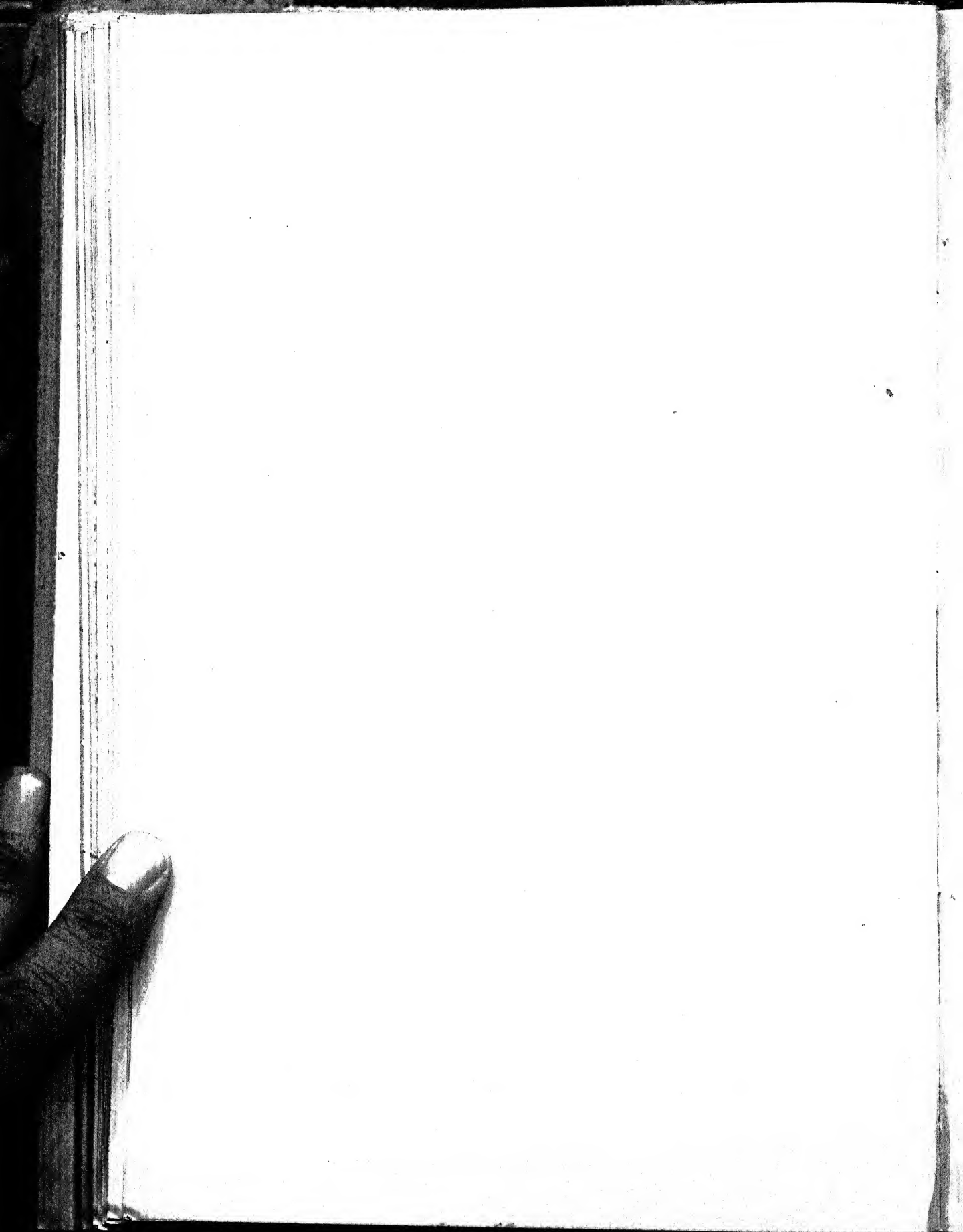
and over 200 new problems. A new chapter in "Recent Researches and Theories" and a few topics and tables have been added, but the general arrangement and scope is unchanged. "Every paragraph has been carefully examined to see if it could be improved," so that the revision has been thorough.

As the textbook is intended mainly for students of agriculture and engineering, the practical applications have been emphasized as is shown in the treatment of the telephone and telegraph, and in chapters on Meteorology, Steam and Gas Engines, Musical Instruments, Optical Instruments, Electrical Measuring Instruments, Dynamo-electric Machines, Electromagnetic Waves and Radiotelegraphy. Recent advances including Discharge of Electricity through Gases and Radioactivity are also presented. Nevertheless, the fundamental theory is presented very fully.

It seems impracticable to get away from the dogmatic method. Thus, we find forces used in statics before the measurement of forces is discussed and then force defined as *ma* before a discussion of the Atwood machine or a statement of Newton's Laws. While for most students such a treatment may not be annoying or confusing, it would not seem to foster a critical scientific attitude nor cultivate intellectual self-reliance. The figures, though not as numerous as in some texts, are well drawn and seem well chosen. On the whole, the book seems well balanced and should serve well as a basis for a thorough course for technical and other serious students.—Pp. xxiii+827, 373 figures, over 600 problems. McGraw-Hill. \$4.00. 1925. G.S.F.

**Mélanges de Mathématiques et de Physiques.** ÉMILE PICARD.—In this volume the permanent secretary of the Academy of Sciences of Paris has gathered together a number of the papers and addresses of Picard on a variety of subjects. Many of the papers deal with the lives and works of celebrated mathematicians, notably Halphen, Weierstrass, Sylvester, Hermite, and Abel. The paper on the solution of the telegraphic equation in the form of an integral equation is included and also a short note on the problem of a disk free to rotate about an axis, the disk carrying a particle moving in a closed curve.

The volume is of interest in showing the breadth of view of the author, a trait which is becoming too rare in these days of specialized effort.—Pp. 364. Paris, Gauthiers-Villars. 25 fr. E. P. ADAMS



# THE PHYSICAL REVIEW

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## PHYSICALLY DEGENERATE SYSTEMS AND QUANTUM DYNAMICS

J. C. SLATER

### ABSTRACT

By analogy with the mathematical definition of degenerate systems, it is suggested that systems which are interrupted before they have traversed a full period, or which are in an external field which varies greatly in the time of one period, be called physically degenerate. It is further suggested, in harmony with the ideas of Ehrenfest and Tolman, that such systems show *weak quantization*, the quantization becoming less and less complete as the degeneracy increases. In the case of partially degenerate systems, the values of the related action variable and of the energy are grouped more or less closely about the mean values which they would all have if the systems were completely quantized. As examples, these ideas are applied to several problems, such as *quantization in a small or rapidly changing magnetic field* (including Glaser's results for the change of diamagnetic susceptibility of some gases with pressure, experiments by Breit and Ellett and by Wood and Ellett on depolarization, and the experiment of Gerlach and Stern in which atoms are projected into a strong field), absorption in the higher lines of the principal series of an alkali (including a discussion of *quantization in hyperbolic and parabolic orbits*), and the continuous x-ray spectrum. It is then pointed out that this assumption demands the *existence of quantum forces* which have not been previously considered in quantum theory and whose action is to stabilize the stationary states, bringing the action variables and energy rapidly nearer and nearer to the proper values as time goes on. The suggestion is made that these forces are responsible for the large change of energy and action variables during a quantum transition. From this point of view the *adiabatic theorem* appears in a simple light; when the external parameters vary too rapidly, the quantization becomes poor, the quantum forces become strong and put the atom into a quantized state again. In any atom but hydrogen, quantum forces must be continuously acting to oppose the interchange of energy and momentum between electrons and to keep each electron quantized. These forces thus may prove to be important in the solution of problems of the quantum dynamics of the constitution of atoms, though they must be considered in connection with the dynamics of the oscillators.

THE quantum theory can hardly continue to deal with periodic systems alone, and the natural approach to the study of non-periodic motion is through those systems which are nearly but not quite periodic. The quantum conditions as at present stated apply only to periodic mo-

tions; it is natural to suppose that nearly but not quite periodic systems are nearly but not quite quantized. One is thus led to the study of weak quantization. The most interesting contributions to this problem have been made by Ehrenfest<sup>1</sup> and his collaborators. In the present paper certain aspects of the problem are discussed from a somewhat different angle from that of Ehrenfest and Tolman, although the underlying ideas are very similar, and, passing beyond their results, an attempt is made to draw certain conclusions regarding quantum dynamics.

#### PART I

Degenerate multiply periodic systems are ordinarily taken to be those in which one or more of the fundamental or combination frequencies are zero for all values of the momenta. In case the vanishing frequencies are combination tones, it is always possible by a change of co-ordinates to make them fundamentals, so that only this case need be considered. Intimately connected with the degeneracy is the failure of the ordinary quantum condition for the variable whose frequency vanishes. For the quantum condition involves an integral about a complete cycle, which is defined only by the motion of the system, and a degenerate co-ordinate, having zero frequency, does not traverse a cycle in any finite time. Thus, for example, an atom cannot be quantized in space unless it is in an external field, for otherwise the frequency of precession of the direction of the angular momentum, one of the fundamental frequencies, is zero, since no torque acts and the axis points in an invariable direction. Then we do not know what a complete cycle for this co-ordinate is; since the axis is fixed, the direction about which it would precess is undefined, and there is no unique way of applying a quantum condition to the orientation. Once there is an external field, however, and the axis does precess in a periodic manner, a cycle is defined and the conditions can be applied.

This statement of the situation seems to imply a distinction between the case where the frequency is strictly zero, and the case where it has any value different from zero. Such a criterion is mathematical rather than physical. In physics one meets with distinctions according as dimensionless quantities are small or large compared with unity. By considering the problem of degeneracy in this light, it can be put in a much more comprehensible form. Instead of considering the mathematical degeneracy of a variable when its frequency is zero, we shall introduce the idea that it is physically degenerate in proportion as the ratio of its

<sup>1</sup> Ehrenfest and Breit, *Zeits. f. Phys.* 9, 207 (1922); Ehrenfest and Tolman, *Phys. Rev.* 24, 287 (1924).

frequency to some fixed quantity of the dimensions of a frequency is small compared with unity.

It is easy to find a fixed quantity having the dimensions of frequency with which to compare the frequency itself. Degenerate systems are of interest principally for two reasons, their lack of quantization under ordinary conditions, and the failure of the quantum conditions to be preserved when the system is carried adiabatically through a degenerate case. We recall that the explanation of the failure of quantization was that the variable never traversed a cycle. It seems reasonable to say that a system is physically degenerate if its variable has had time to go through only a part of a cycle. The fraction of a cycle which has been passed through since any given instant is the product of the frequency and the length of time which has elapsed, or the ratio of the frequency to the reciprocal of that time. It is then very reasonable to define a physically degenerate system as one in which one of the frequencies is small compared with  $1/T$ , where  $T$  is the length of time in which the motion has been going on. If the motion has been progressing since the atom entered its stationary state, then the average value of  $T$  is the average life in the state, or  $1/T$  is the probability of leaving the state in unit time, which has the dimensions of a frequency.

Degenerate systems are of particular importance, also, in the application of the adiabatic theorem; for as an external parameter is varied slowly, the quantum conditions are continually satisfied, except in the very important case in which the system passes through a degenerate state. For the theorem to hold, the external parameter must vary so slowly that it remains approximately constant over one period; but if one of the fundamental frequencies becomes very small, a period of that frequency is very large, and if the external parameter changes at any reasonable rate it will change decidedly during one period, so that the conditions of the theorem are not met. Evidently, in this case, a definition of physical degeneracy is immediately provided: A system is physically degenerate if the external field changes so fast that the adiabatic theorem does not hold. This amounts to saying that the product of the relative change in the parameter per unit time, and the time of one period, is large; or that the ratio of the frequency to the relative change of the parameter per unit time is small. This is the same kind of condition we had before; but now  $T$  is the reciprocal of the relative change of the external parameter per unit time; that is, it is the time in which the parameter changes by an amount comparable with itself. If, for example, the parameter varies periodically,  $1/T$  is a small constant times the frequency of variation.



Suppose that physical degeneracy be defined as just suggested, for the two cases of interrupted motion and of motion in a varying field. We then meet the problem of quantization. The conventional statement is that mathematically degenerate systems are not quantized; undegenerate ones are. This, again, is an unphysical sort of definition; and we amend it to say that the completeness of quantization approaches zero with the quantity  $\nu T$ ,  $\nu$  being the frequency in question; that is, the quantization is less and less complete in proportion as the system is more and more degenerate physically. This statement covers both cases we have considered. We ask more closely as to the meaning of the completeness of quantization. When quantization of a particular co-ordinate is complete, all systems have one or another of a set of definite values for the phase integrals, or action variables, connected with that co-ordinate; when there is no quantization, the various systems have values of the related action variable which are spread in a uniform fashion over a large range of values. An intermediate state of quantization would be one in which, while all systems do not have precisely the same values of the action variables, still they are grouped more or less closely about the mean values. Thus it is to be supposed that, as  $\nu T$  increases, the systems, having for  $\nu T=0$  all values of the action variable associated with the frequency  $\nu$ , have their values of action cluster closer and closer together until finally for  $\nu T=\text{infinity}$ , all have precisely the same value. Now the energy of a system is a function of the action variables; so that, if, with incomplete quantization, there are systems with many values of the action variables, there are also systems with a variety of energies. Thus, as  $\nu T$  increases, the energies draw closer and closer together, if we leave out of account the effect which the incomplete quantization of other variables would have on the energy. This diffuseness of energy values results, if we apply Bohr's frequency condition, in a diffuseness of the resulting spectral lines; and this may be connected with the diffuseness in the spectrum of the oscillators producing the radiation, on account of their finite time of oscillation. This connection will not, however, be discussed in the present paper.

A number of examples will illustrate the many applications of these ideas to familiar problems of quantum theory. Perhaps the most complete example is the problem of quantization in a magnetic field. Let us first consider a static magnetic field. Then  $T$  represents the length of life of a stationary state, or  $1/T$  equals on the average the probability  $P$  of leaving the state. The frequency which may become degenerate is the frequency of precession; it is the Larmor frequency  $eH/4\pi mc$  if the Zeeman effect is normal, or a small number times this if it is anomalous. This frequency

vanishes with  $H$ , the external magnetic field. The associated action variable is the component of the angular momentum in the direction of  $H$ ; and since the total angular momentum is independent of the field, this amounts to a constant times the cosine of the angle between the axis of the atom and  $H$ . Our statement is now that the strength of the quantization is measured by  $(eH/4\pi mc)/P$ , which equals the average number of cycles which the Larmor precession makes in the time of a stationary state. When, then,  $H$  is small, the quantization becomes poor. That is, the directions of the axes cease to be assigned to definite values, but are merely clustered about those values as most probable ones. In the limit, when  $H$  is zero, the emphasis on the "quantized" directions is completely lost, the distribution of directions being entirely at random; and the range of values of  $H$  in which the change occurs is that region where it is of the same magnitude as  $4\pi mcP/e$ . If, then, we are to take a constant field and increase  $P$ , the probability of leaving the stationary state, the direction of orientation becomes less and less quantized until finally it is not quantized at all. An interesting experimental application of this result appears to be the discovery of Glaser<sup>2</sup> on the change of the diamagnetic susceptibility of some gases with pressure. Glaser finds that the magnetic susceptibility of certain gases decreases from one definite value to another when the pressure is increased at constant magnetic field, the change coming in a rather sharply defined pressure range. This he interprets as a change from a quantized condition at lower pressures to a non-quantized one at higher pressures, the oriented molecules having a greater diamagnetic effect than those oriented at random. Now increasing the pressure increases the probability of collision, and it seems inevitable that a collision would disturb the periodicity of the precession, so that we can consider the time  $T$  to be the average time between collisions, and  $P$  the probability of collision. Then we see that increasing  $P$  should, in fact, decrease the completeness of quantization and hence the susceptibility. Further, the range of values of  $P$  in which the change should come for a given value of  $H$ , can be found from the formula above; and if we calculate by gas theory the pressures for which the probability of collision is of this order, we find closely the range of pressures actually determined experimentally by Glaser. It is also found by Glaser that the range of pressure, and hence  $P$ , increases with increasing magnetic field, as we should expect.

We may also consider the case of the quantization in a variable magnetic field. The simplest case is that of a periodically varying field. Here we shall expect the quantization to begin to fail, for constant  $H$

<sup>2</sup> Glaser, *Ann. der Phys.* **75**, 459 (1924).

and increasing frequency of the field, when the frequency of the field approaches that of the Larmor precession, for the frequency of the field is of the same order as the relative change of the field in unit time. This case appears to find an application in the recent experiment of Breit and Ellett<sup>3</sup> on the depolarization of resonance radiation by an oscillating magnetic field. Wood and Ellett<sup>4</sup> find that the depolarizing effect of a steady field increases as its Larmor precession becomes of the same order of magnitude as the probability of leaving the excited state, so that this effect is apparently connected with the strength of the quantization of the excited state. Breit and Ellett then take a field which is just strong enough to depolarize, but have it of an oscillating frequency. So long as its frequency of vibration is small compared with the probability of leaving the state, it depolarizes; but when its frequency becomes greater than the probability, the depolarizing effect decreases. This would be interpreted by saying that in the first case the time  $T$  was the time of a stationary state, and hence unaffected by the field, while in the second case it was the shorter time in which the field remained approximately constant, which decreased in inverse ratio to the frequency. Since the Larmor frequency is kept throughout of the order of magnitude of the initial  $1/T$ , the depolarizing effect is unchanged until the stage is reached where the fluctuations of the field predominate over the probability of leaving the stationary state, in dequantizing effect. Then  $T$  and  $\nu T$  begin to decrease, and this seems to be what is necessary to destroy the depolarization. Thus this phenomenon is in harmony with the view that a limitation of  $T$ , either by variation of the external parameters or by limiting the life in the stationary state, has the same effect.

Another case of quantization in a magnetic field is the experiment of Stern and Gerlach.<sup>5</sup> Here silver or other atoms are produced with a considerable thermal velocity in a region of practically no magnetic field and are then shot suddenly into a strong and variable magnetic field. As they enter the field they are presumably unquantized, for the Larmor frequency in the stray fields they had previously been in was not great enough to produce quantization. An approximately constant

<sup>3</sup> Briet and Ellett, *Phys. Rev.* **25**, 888 (abstract) (1925).

<sup>4</sup> Wood and Ellett, *Proc. Roy. Soc. A* **103**, 396 (1923);

Eldridge, *Phys. Rev.* **24**, 234 (1924); and particularly Breit, *Phil. Mag.* **47**, 832 (1924). Breit (*loc. cit.*, p. 840) adopts precisely the present point of view regarding the diffuseness of quantization in weak fields.

<sup>5</sup> For general description of method, see Gerlach and Stern, *Ann. der Phys.* **74**, 673 (1924).

field is then suddenly applied to them; its magnitude is of the order of 12,000 gauss, so that its Larmor frequency is of the order of  $1.7 \times 10^{10}$  per sec. At any subsequent instant, then, the time  $T$  will be the time which has elapsed since entering the field, or the time in which the field where the atom is changes by a considerable fraction of itself, whichever is smaller, and the strength of quantization will depend on  $\nu T$  or  $1.7 \times 10^{10} T$ . If, then,  $T$  is large compared with  $6 \times 10^{-11}$  sec., the atom will be well quantized. Now the velocity of the atom is the thermal velocity, of the order of  $5 \times 10^4$  cm/sec., so that if the field is 5 cm long, it takes  $10^{-4}$  sec. to traverse it. This, then, is the order of the time required for the field at the atom to change by a large fraction of itself, so that the process is perfectly adiabatic as far as the change of the field is concerned, except, perhaps, at the very beginning, when the atom suddenly enters the field. The quantization would be expected to be good except for the insignificant time of the order of  $6 \times 10^{-11}$  sec. just at the beginning.

Quantization in a magnetic field forms the best example of a degenerate system as it is the most familiar, but many other less familiar cases are no less significant. For example, suppose we are considering hydrogen atoms in various excited states. Corresponding to each total quantum number, there are, if the relativity precession be considered, states with various azimuthal quantum numbers. If each atom existed an infinite time in its stationary state, they would all have precisely one or another of the "allowed" values of angular momentum; but now suppose the life of the stationary states to be decreased, by increasing the pressure or by some other method; then the ratio of the relativity precessional frequency to the probability of leaving the state decreases. Thus the quantization decreases and the values of angular momentum and of the minor axes of the elliptical orbits are no longer confined to definite values but are distributed over all values, clustering, however, about these as means. Finally, as the life gets very short—so short that but a fraction of a complete precession is made in one stationary state—the angular momentum is distributed evenly over all possible values, with no clustering at all about the multiples of  $h/2\pi$ .

Another case is furnished by absorption in the higher lines of the principal series of an alkali. There the excited orbits are very eccentric and of frequency decreasing as the principal quantum number increases, until for an infinite quantum number the frequency becomes zero, the orbit becoming parabolic. But, in the limit, the life remains finite under ordinary circumstances, so that a point must be reached in the scale of ascending quantum numbers, above which the fundamental frequency is small compared with the probability of interruption, and the electron

makes only a part of a circuit of its orbit before it is interfered with. At this point, then, the quantization must become diffuse, so that for greater values a continuous range of energies and angular momenta is possible. As we pass to the parabolic orbit, the tendency to quantize completely disappears. This case differs from the previous ones in that here all variables become degenerate, the largest frequency vanishing and periodicity ceasing. When this stage is reached, it is a transition only of degree, not of kind, to the hyperbolic orbits, which may likewise be supposed to be interrupted after finite lengths of time; a finite part of a hyperbolic orbit is not different in kind from a finite part of an ellipse. It appears from this that hyperbolic orbits should show no indication of sharp quantization. This situation would find application in the related problems of the continuous absorption beyond the limit of the series, and the continuous x-ray spectrum. In the first case, the final orbit is supposed to be of hyperbolic type; hence its action variables and energy are distributed continuously, and by the frequency relation the absorption spectrum is continuous. In the second case, the initial state consists of a free electron and an ion or atom, so that the electron may be considered to be describing an orbit of generally hyperbolic nature; and the final orbit is presumably sometimes of the same kind, sometimes an elliptic, quantized orbit. As in the orbits of hyperbolic type, we should expect that there would be complete absence of quantization in any other completely non-periodic type of motion which appears as the limiting case of complete physical degeneracy. A free electron in a metal, for example, if it really bumps about from atom to atom, must be expected to show practically no quantization of the ordinary kind. An extension of the ideas described here seems to offer the most hopeful method of attack on the problems of non-periodic motion in the quantum theory.

## PART II

The suggestion that the strength of quantization depends on  $\nu T$  carries an implication of greatest importance in regard to quantum dynamics. Assume a collection of atoms which at a given instant enter a stationary state, and suppose that none of them have anything to interfere with their periodicity for some time after that. Then, after a time  $T$ , the average strength of quantization will depend on  $\nu T$ ; but this increases with the time, so that the quantization must become better and better as time goes on. That is, the energy and momentum of the various systems must cluster closer and closer about mean values with increasing time. As a necessary result, the energy and momentum of any individual atom must move closer and closer to the perfectly quantized value as time

goes on. After a short enough time interval, any co-ordinate can be regarded as degenerate, while after a time of the order of a few vibrations of the principal frequency, the principal variables become properly quantized. This implies a mechanism by which the energy and action variables can be varied, wholly apart from classical mechanics, and varied in such a way as to bring them nearer and nearer to quantized values. Since the energy and momentum are generally considered to be changed only by the action of forces, it must be supposed that there is a quantum mechanism which exerts essentially a stabilizing force, pulling the systems into their properly quantized orbits. This is a conception very different from the conventional one, by which the quantum part of atomic dynamics is considered simply as a restriction on the constants of integration of the orbits. Nevertheless, it seems to be demanded by many things.

Perhaps the best example of the need of some such extra-mechanical force is seen in Stern and Gerlach's experiment where atoms from a region where there is no magnetic field, or at least where the magnetic field is so small and so rapidly changing that atoms will not be quantized in it, suddenly emerge into a strong field. They will be originally oriented in all directions, and hence will have all values of magnetic energy. Yet when the atoms are quantized—which in the experiment actually happens—they have definite values of energy, so that each must have gained or lost in the process of quantization, energy comparable with its whole magnetic energy. This is an amount much greater than can be gained or lost in this time by mechanical means. Einstein and Ehrenfest<sup>6</sup> have calculated the change of magnetic energy classically, on account of the radiation accompanying the Larmor precession, and find it of an order of magnitude altogether too small to account for the comparatively large and sudden change. This fact they consider a serious difficulty connected with the experiment, but it is a perfect example of the present theory, and the change of energy involved in orientation is to be thought of as produced by the quantum forces which we have introduced.

It is possible to apply the conception in a more ambitious way: to the dynamics of quantum transitions. As an atom enters a stationary state, we should expect according to our theory that its energy and action variables can have values anywhere inside a wide range. Is there any objection to supposing that they may have the values which they had as they left the last state? There does not seem to be. It seems permissible to suppose that the part of the change of stationary state

<sup>6</sup> Einstein and Ehrenfest, *Zeits. f. Phys.* 11, 31 (1922).



which occurs instantaneously is not the change in energy and action variables, but the change in the orbit toward which the stabilizing forces impel the atom. If the atom is well quantized in an orbit, so that these forces are not active, and there is a sudden change in the orbit toward which the forces are acting, the atom will find itself very badly quantized, and the forces will suddenly commence to act violently. In the course of a few vibrations, however, any given action variable will be forced to approximately its proper value, which will be approached more and more closely as time goes on. On this view, the energy and action variables would change continuously; the two kinds of action, transitions and stationary states, which have previously been considered as entirely separate, would appear simply as two aspects of the same kind of dynamical action, the transitions being the periods when the quantum forces are very active, the stationary states when they are relatively quiescent. The lower a frequency is, the longer would take the transitional part of its motion, and for a frequency of the kind we have called degenerate, the variable would be always in a situation of transition, never reaching a real stationary state—whose characteristic would be the completeness of the quantization. In a system that is degenerate in all its variables, so that the orbit toward which the quantum forces impelled the motion changed in a time comparable with a period, the quantum forces would be continually active, never becoming quiescent, so that such a motion would be completely inexplicable on classical dynamics. The free electron in its interaction with an atom would be an example of this.

The adiabatic theorem, and the cases when it breaks down, appear in a simple light. If an external parameter varies slowly, then at any instant the variables have all gone through many vibrations since their periodicity was appreciably affected, so that the quantization is good, remains good, and the quantum forces remain small. The classical forces alone, as is known, are enough in this case to produce the changes in the orbit. As soon, however, as the external parameters vary too rapidly, the quantization ceases to be good, the quantum forces become strong and attempt to pull the atomic system back to its original stationary state or into some other. In this situation, the ordinary dynamical forces are known no longer to tend to keep the action variables constant, but to vary them, so that if only the classical forces acted, the system would become permanently unquantized if a parameter varied suddenly. With the quantum forces, however, the effect is much like a quantum transition and results in the atom going to a quantized state again. All intermediate stages between the adiabatic and the transition-like action would occur, with different grades of suddenness of change of the conditions.



The quantum forces which have been suggested may be applied, by virtue of one of their simplest properties, to some of the difficult problems of quantum dynamics. Their aim appears to be to get the atom in a quantized state, which is a multiply periodic motion with proper values for the action variables, and to keep it there; their action is roughly analogous to a sort of restoring force for atoms that stray from their proper orbit, so that they must be supposed to oppose any force which tries to remove the atom from a quantized orbit. Of course, in speaking of force, the word is used in the sense of generalized co-ordinates, and not as forces literally acting toward definite points of the path. In hydrogen, the coulomb forces and the relativity forces are capable of maintaining the atom in a multiply periodic, quantized orbit. Thus, when the atom remains in its stationary state, the quantum forces do not oppose the classical ones. Likewise they do not oppose external fields, such as constant or slowly changing magnetic or electric fields, which would also result in quantized orbits; but the radiation resistance, and the forces from external radiation fields, both do tend to change the atom's action variables. They must then be expected to be opposed by the quantum force, which will not allow them to affect appreciably the motion of the system. Since the quantum forces must be supposed capable of exerting powerful action, they are presumably able completely to counteract the effect of such forces. The reaction of such effects on the quantum forces appears in quite a different way, namely, in the induction of quantum transitions.

For any atom but hydrogen, if we consider only classical forces and consider each electron as a system by itself, to be quantized by itself, there are large classical forces tending to change the energy and action variables of each separate electron; for in the interaction of electrons, if it is classical, energy passes from one electron to another during the cycle. In such a system, then, powerful quantum forces are set up tending to oppose this interchange of energy, angular momentum, etc., between the various electrons, and tending to force the individual electrons into multiply periodic orbits, each quantized by itself. If the quantum forces succeed in this, they will still have to act all during the motion, opposing some of the classical forces. But the result will be exactly the kind of motion which we believe occurs in atoms—multiply periodic motion of the single electrons, with no interchange of energy or other quantities between the different parts of the atom in the course of the stationary state; that is, just the kind of motion we should have if each electron were in a central field. A hint is thus given of the direction in which to approach the problems of atomic dynamics, namely, the introduction of quantum forces, opposing some of the classical forces,

and allowing only those to act which help to maintain each separate electron in multiply periodic motion. Only in the case of hydrogen do the forces necessary to do this become vanishingly small, so that only in this case can we expect the classical dynamics to provide a basis for discussing stationary states; and even in this case we cannot expect to discuss the stability of the orbits by classical mechanics.

In spite of the apparent hopefulness of this line of attack on quantum dynamics, it would be foolish to suppose that it was sufficient in itself to solve the problem; for it must be recalled that the dynamics of stationary states represents but one of the two aspects of atomic mechanics, the other being the dynamics of the oscillators, each connected with two stationary states. In hydrogen, the Bohr atom has shown that the dynamics can be discussed with great ease from the first standpoint, and this leads one to the conviction that such a treatment is possible in other cases also. But there are reasons for believing a discussion to be possible on the second basis also, and for thinking that that might be simpler than the first for complicated atoms; for the action of an external oscillating electric field of optical frequency on an atom is most simply treated by considering the oscillators directly, and in an atom of more than one electron, the field of one electron on another is probably of this form. Thus it seems reasonable to suppose that we could consider the dynamics of such an atom by treating the reactions of the oscillators connected with the various electrons on each other directly. Such an idea was in the mind of the author when he suggested a mechanism of oscillators to describe the reaction of an atom to light; it has occurred also to Born<sup>7</sup> and presumably to others. It seems probable that both of these methods of attack on quantum dynamics will prove fruitful, and will eventually be found to be related. The most useful method of procedure seems to be to work on both methods together, trying to fit them into a single consistent scheme, the connection between them being presumably in the nature of extensions of the frequency condition and the correspondence principle.

In a subject which has been thought about by as many physicists as this undoubtedly has, it is naturally impossible to claim much originality, in spite of the small amount which has been written about it specifically. I have had the pleasure of discussing certain parts of this paper with Dr. Breit, who holds very similar opinions to mine on most of the questions. My thanks are due, also, to Professor P. W. Bridgman for valuable suggestions regarding quantum dynamics, and to Professor E. C. Kemble and Dr. L. A. Turner for their criticisms.

JEFFERSON PHYSICAL LABORATORY,  
June 8, 1925

<sup>7</sup> Born, *Zeits. f. Phys.* 26, 379 (1924).

## ON THE ESTIMATION OF MAXIMUM COEFFICIENTS OF ABSORPTION

BY RICHARD C. TOLMAN

## ABSTRACT

On the basis of the correspondence principle it is shown that Einstein's coefficient of absorption can be estimated from the equation  $B_{na} = 2\pi^2 e^2 Q^2 / 3\hbar^2$  where  $e$  is the charge and  $Q$  the amplitude of the virtual oscillator which corresponds to the transition by absorption from state  $S_n$  to  $S_a$ . Assuming that probable maximum values can be obtained by taking  $e$  equal to the charge of one electron and  $Q$  equal to  $3 \times 10^{-8}$  cm, we obtain  $(B_{na})_{\max} = 10^{20}$  in c.g.s. units, in agreement with values from  $10^{14}$  to  $2.3 \times 10^{19}$  previously calculated by the author from absorption data.

IN connection with theories of the rates of chemical reactions, it is important to estimate the maximum values which we are likely to encounter for the coefficient of absorption of light by molecules.<sup>1</sup> The recent work of Van Vleck<sup>2</sup> on the form taken by the Bohr correspondence principle when applied to absorption, and of Hoyt<sup>3</sup> and the present writer<sup>4</sup> on the problem of the quantitative formulation of the correspondence principle, suggest a somewhat new approach to this question.

Consider two of the possible quantum states of a molecule, a lower (normal) quantum state  $S_n$  and an upper (activated) quantum state  $S_a$ , and let us investigate the passage of molecules from one of these states to the other by the absorption and emission of radiation. If we have  $N_a$  such molecules in the upper quantum state, the rate of spontaneous emission of energy due to the jump in question will have, on the basis of the *quantum theory*, the value

$$dR/dt = N_a A_{an} h\nu \quad (1)$$

where  $A_{an}$  is Einstein's coefficient giving the probability in unit time for the spontaneous emission of a quantum  $h\nu$ .

In order to apply the correspondence principle, let us now proceed in a manner which may for the moment seem somewhat arbitrary, and equate this rate of energy emission to the quantity

$$dR/dt = N_a (16\pi^4 e^2 / 3c^3) Q^2 \nu^4 \quad (2)$$

which is the rate of emission on the basis of the *classical theory* of a set of

<sup>1</sup> See for example Tolman, J. Amer. Chem. Soc. **47**, 1524 (1925).

<sup>2</sup> Van Vleck, Phys. Rev. **24**, 330 (1924).

<sup>3</sup> Hoyt, Phil. Mag. **46**, 135 (1923); *ibid.*, **47**, 826 (1924).

<sup>4</sup> Tolman, Phil. Mag. **49**, 130 (1925).

harmonic electric oscillators of charge  $e$ , frequency  $\nu$ , and amplitude  $Q$ . We obtain for Einstein's coefficient of spontaneous emission the expression

$$A_{an} = (16\pi^4 e^2 / 3hc^3) Q^2 \nu^3 \quad (3)$$

and by substituting the known relation

$$A_{an} = (8\pi h \nu^3 / c^3) B_{na} \quad (4)$$

between Einstein's coefficients of absorption and emission can obtain for the coefficient of absorption the expression

$$B_{na} = (2\pi^2 e^2 / 3h^2) Q^2 \quad (5)$$

where the desired quantity  $B_{na}$  is the chance per unit time that a molecule in state  $S_n$  will pass to the upper state  $S_a$  by absorption, when in the presence of radiation of unit density.

On the basis of the *correspondence principle*, however, we should expect the amplitude  $Q$ , which was introduced above in a seemingly artificial manner, to be calculable as an average of the corresponding amplitude present in the classically allowed motions of the molecule, which lie between the two quantum states  $S_n$  and  $S_a$ . Different methods of taking this average have been studied by Hoyt and the present writer, and the exactly correct method has not yet been determined. Nevertheless, since in accordance with Bohr's correspondence principle  $Q$  is the amplitude of that particular harmonic in the internal motion, having order numbers  $\tau_1 \dots \tau_s$  equal to the changes in quantum numbers  $\Delta n_1 \dots \Delta n_s$  which characterize the quantum transition in question, we should expect that a reasonable estimate of the probable maximum values of  $B_{na}$  could be obtained by taking  $Q$  of the order of molecular dimensions.

As a matter of fact, giving  $Q$  the value of  $3 \times 10^{-8}$  cm and assuming the charge  $e$  of the oscillating system to be that of one electron, we obtain from Eq. (5) the value  $B_{na} = 10^{20}$  c.g.s. units. It is interesting to compare this estimated maximum with the values of  $B_{na}$  calculated by the author<sup>5</sup> from actual absorption measurements in a variety of cases where data were available. The values obtained ranged all the way from  $10^{14}$  to  $2.3 \times 10^{19}$  c.g.s.u., which are not out of accord with the above estimate.

In connection with the foregoing treatment, attention is called to the advantage obtained by using Eq. (5) to estimate possible values of  $B_{na}$ , rather than Eq. (4) to estimate values of  $A_{an}$ , since in this way we obtain a quantity which is independent of the frequency. This new possibility was suggested to the writer by Van Vleck's work.

NORMAN BRIDGE LABORATORY OF PHYSICS,  
CALIFORNIA INSTITUTE OF TECHNOLOGY,  
PASADENA,  
June 24, 1925.

<sup>5</sup> Tolman, Phys. Rev. 23, 699 (1924).

THEORY OF THE NUMBER OF BETA-RAYS ASSOCIATED  
WITH SCATTERED X-RAYS

BY G. E. M. JAUNCEY AND O. K. DEFoe

## ABSTRACT

In a recent paper by Compton and Simon the ratio of the number of recoil electron tracks to that of photo-electron tracks has been found equal to the ratio of scattering coefficient  $\sigma$  to true absorption coefficient  $\tau$  for short wave-length x-rays, as predicted by Compton and Hubbard, but for long wave-lengths the experimental ratio is distinctly smaller. In the present paper a correction factor is applied to  $\sigma/\tau$  by taking into account the motion and the binding energy of the scattering electron in its Bohr orbit and also the minimum energy which the recoil electron must have in order to produce a visible track in a Wilson cloud apparatus. Assuming a minimum energy of 630 volts for a recoil electron to produce a visible track, the correction factor for a primary wave-length of 0.71A is 0.36, thus making the theoretical value of the ratio of recoil to photo-electron tracks 0.097 as against an experimental value of 0.10. For other wave-lengths the agreement is equally good.

## INTRODUCTION

A. H. COMPTON AND SIMON<sup>1</sup> have recently published a paper on the beta-rays associated with scattered x-rays. They counted the beta-ray tracks in a Wilson cloud apparatus. Two types of tracks are in general produced, the R type, which are short tracks and are due to recoil electrons, and the P type, which are longer and are due to photo-electrons. Compton and Hubbard<sup>2</sup> have shown for the case of scattering by free electrons that the ratio of the number of R tracks to that of the P tracks is given by

$$N_R/N_P = \sigma/\tau \quad (1)$$

where  $\sigma$  is the scattering coefficient and  $\tau$  the true absorption coefficient of the x-rays in the gas in the expansion chamber. In Table I of the paper by Compton and Simon<sup>1</sup> values of  $N_R/N_P$  as observed experimentally are compared with values of  $\sigma/\tau$  and a very good agreement is shown when short wave-length x-rays are used. For long wave-length x-rays, however,  $N_R/N_P$  is distinctly smaller than  $\sigma/\tau$ . Compton and Simon point out that the reason for this discrepancy may be that the spectrum of scattered x-rays shows both a modified and an unmodified line and that the latter is probably the result of scattering without the production of a recoil electron, but they remark that the accuracy of their counting becomes small at long wave-lengths and that therefore the discrepancy

<sup>1</sup> A. H. Compton and A. W. Simon, Phys. Rev. **25**, 306 (1925).

<sup>2</sup> A. H. Compton and J. C. Hubbard, Phys. Rev. **23**, 439 (1924).

may be due to experimental error. Jauncey's theory of the unmodified line<sup>3</sup> requires that unmodified scattering should occur without the production of recoil electrons.

### THEORY

On Jauncey's theory,<sup>3</sup> the ratio of the number of modified quanta scattered at an angle  $\phi$  to the total number of quanta scattered at this same angle for the case where the binding energy of the scattering electrons is small and the electrons are moving in circular orbits is

$$\frac{N_{mod}}{N_{total}} = \frac{a_0 \text{ vers } \phi + 2\sqrt{2a_s} \sin \frac{1}{2}\phi - \lambda_0/\lambda_s}{4\sqrt{2a_s} \sin \frac{1}{2}\phi} \quad (2)$$

where  $\lambda_0$  is the wave-length of the primary x-rays,  $\lambda_s$  a critical absorption wave-length of the scattering substance,  $a_0 = h/mc\lambda_0$  and  $a_s = h/mc\lambda_s$ .

Next we must consider the fact that all of the recoil electrons do not possess sufficient energy to produce noticeable recoil tracks. C. T. R. Wilson<sup>4</sup> gives a formula  $V = 21000\sqrt{R}$  where  $V$  is the energy of an electron in volts and  $R$  is the range of the track produced in centimeters. Probably the length of the shortest track which could be distinguished would be of the order of 1/100 mm. Such a track would be produced by electrons of 630 volts. The track would probably appear as a sphere track. It may be mentioned that Miss Anslow<sup>5</sup> gives it as her opinion that the sphere tracks observed in Wilson's photographs are produced by 998 volt electrons. Hence, our assumption of 630 volts is of the right order of magnitude. An energy of 630 volts corresponds to the energy of a quantum of wave-length 20A. Let us denote this wave-length by  $\lambda_i$ . The energy of a recoil electron is  $hc(1/\lambda_0 - 1/\lambda_\phi - 1/\lambda_s)$  and this must be at least  $hc/\lambda_i$  in order to produce a visible track. Hence, at least

$$\lambda_\phi/\lambda_0 = (1 + \lambda_0/\lambda_s + \lambda_0/\lambda_i) \quad (3)$$

since both  $\lambda_s$  and  $\lambda_i$  are much larger than  $\lambda_0$ . The effect of Eq. (3) is to replace  $\lambda_0/\lambda_s$  in the numerator of the right hand member of Eq. (2) by  $(\lambda_0/\lambda_s + \lambda_0/\lambda_i)$  in the expression for the ratio of the number of visible recoil electrons to the total number of quanta scattered at the angle  $\phi$ . Hence, this ratio is

$$X = \frac{N(\text{recoil})}{N(\text{quanta})} = \frac{a_0 \text{ vers } \phi + 2\sqrt{2a_s} \sin \frac{1}{2}\phi - \lambda_0/\lambda_s - \lambda_0/\lambda_i}{4\sqrt{2a_s} \sin \frac{1}{2}\phi} \quad (4)$$

<sup>3</sup> G. E. M. Jauncey, Phys. Rev. **25**, 314 (1925).

<sup>4</sup> C. T. R. Wilson, Proc. Roy. Soc. **104**, 1 and 192 (1923).

<sup>5</sup> G. A. Anslow, Phys. Rev. **25**, 484 (Apr. 1925).

In order to find the average value of  $X$  when integrated over all angles of scattering it is necessary to know the angular distribution of the scattered quanta. We shall assume as an approximation the distribution given when the electrons are free. The theories of A. H. Compton<sup>6</sup> and Jauncey<sup>7</sup> give

$$N_{\phi} = \text{const.} \times \frac{1 + \cos^2 \phi + 2a_0(1 + a_0) \text{vers}^2 \phi}{2(1 + a_0 \text{vers} \phi)^4}. \quad (5)$$

The average ratio is then

$$k = \frac{\int_0^{\pi} N_{\phi} X \sin \phi d\phi}{\int_0^{\pi} N_{\phi} \sin \phi d\phi}. \quad (6)$$

It should be noted that  $X$  is taken as zero when the right hand member of Eq. (4) is negative and as unity when the right hand member exceeds unity. For scattering by a particular type of K, L, etc., electrons, the experimental ratio  $N_R/N_P$  should be given by  $k\sigma/\tau$ . For scattering by air  $k$  must be averaged for the different types of electrons and the different atoms. These averaged values of  $k$  calculated on the assumption that  $\lambda_i = 20\text{\AA}$  are shown in Table I.

TABLE I

Wave-length	$N_R/N_P(\text{obs.})$	$\sigma/\tau$	$k$	$k\sigma/\tau$
.71A	.10	.27	.36	.097
.44	.9	1.2	.62	.75
.29	2.7	3.8	.82	3.1
.20	9.0	10.	.90	9.0
.17	17.	17.	.92	15.6
.13	72.	32.	.95	30.4
.024	.....	.....	.995	.....

The first three columns are taken from Table I of Compton and Simon's paper.<sup>1</sup> It is seen that there is better agreement between the second and fifth columns than between the second and third columns.

WASHINGTON UNIVERSITY,  
ST. LOUIS, MISSOURI,  
April 29, 1925.

<sup>6</sup> A. H. Compton, Phys. Rev. **21**, 483 (1923).

<sup>7</sup> G. E. M. Jauncey, Phys. Rev. **22**, 233 (1923).



# PROBABILITY OF IONIZATION OF GAS MOLECULES BY ELECTRON IMPACTS

BY K. T. COMPTON AND C. C. VAN VOORHIS

## ABSTRACT

Ionization in various gases by electrons of energy 0-325 volts.—Electrons from a hot filament were projected through an ionization chamber *B* containing gas at low pressure (.001 to .005 mm) and into a trap. Positive ions produced in *B* were collected on fine wires arranged in the form of a squirrel cage *C* and maintained at a potential lower than *B* by an amount  $V_r$ . Corrections were made for the facts (1) that the wires *C* lowered the potential at the center of *B* and hence retarded the electrons passing through *B* by a maximum amount of  $0.4 \times V_r$ , and (2) that if  $V_r$  was numerically less in value than the accelerating potential  $V_a$ , some primary electrons reached *C*. The pressures were measured with a McLeod gauge to 1 percent and were corrected for the heating effect of the filament, which was determined by using the apparatus as an ionization manometer to be about 26°. The resulting curves for *N*, the number of ions per cm path produced by an electron moving through a gas at 1 mm pressure, are believed correct within a few percent. In agreement with previous results of Hughes and Klein and others, the curves each rise to a maximum. The maximum values found and the corresponding voltages are as follows:

	H <sub>2</sub>	He	Ne	A	N <sub>2</sub>	Hg	HCl
<i>N</i> (max):	3.55	1.65	3.2	10.33	9.96	19.44	17.3
<i>V</i> (max):	145	210	340	140	175	135	130
<i>P</i> (max):	0.29	.209	.254	.466	.423	.239	.558

The values for *P*(max), the corresponding probability that a collision will result in ionization of the hit molecule, were computed from *N*(max) assuming the kinetic theory values for electronic mean free paths. These results are compared with previous experimental values. Ionization was found to begin at the ionizing potential in each case, except that with N<sub>2</sub> weak ionization was observed at 10 volts. This may possibly be associated with the presence of traces of active nitrogen.

TOWNSEND'S original theory of ionization by collision<sup>1</sup> assumed that ionization of a gas molecule occurs whenever it is struck by an electron whose speed exceeds the minimum ionizing speed, but this theory led to values of the minimum ionizing speed which were considerably in error. Bergen Davis<sup>2</sup> and one of the writers<sup>3</sup> modified Townsend's theory by assuming that the relation between the energy *V* of an electron at impact and the probability *P* that ionization of the molecule results from the impact is given by  $P = (V - V_i)/V$  when  $V > V_i$  and  $P = 0$  when

<sup>1</sup> Townsend, "The Ionization of Gases by Collision."

<sup>2</sup> Bergen Davis, Phys. Rev. 24, 93 (1907).

<sup>3</sup> K. T. Compton, Phys. Rev. 7, pp. 489, 501, 509 (1916); Compton and Benade, ibid. 11, 234 (1918).

$V < V_i$ . This assumption led to calculated values of the minimum ionizing energy  $V_i$  which agreed better with the true values than did Townsend's original theory, but which were still incorrect. The recent advances in the study of various types of electrical discharge through gases, and especially the development of Langmuir's<sup>4</sup> new method for determining the distribution of velocities of the electrons in an ionized gas, have emphasized the importance of accurate knowledge of the values of the probability  $P$  of ionization by electron impacts at various speeds and in various gases.

The first experimental observations of this sort were made by Lenard<sup>5</sup> and were extended under his guidance by Kossel<sup>6</sup> and Mayer.<sup>7</sup> These investigators found that the probability of ionization is zero for impact energies up to the minimum ionizing potential, then increases to a maximum of less than 0.5 at impact energies of about 150 volts, followed by a decrease as the energy is further increased up to 1000 volts.

The present investigation was designed to introduce a number of refinements in technique, so as to permit the maximum possible accuracy of the observations. Shortly after we had begun, Hughes and Klein<sup>8</sup> published results of a research on the same problem, in which a considerable number of gases was tested over a large range of electron impact energies. In general features and in order of magnitude our present results agree with the findings of these and of the earlier investigators. We believe, however, that the present method permits greater accuracy of observation and reliability of interpretation than the methods previously used, so that we felt justified in continuing the work to its present conclusion.

The general procedure in such work is to accelerate electrons from a photo-electric or thermionic source and project them into a region in which the products of ionization are collected by a subsidiary system of electrodes. Besides obvious precautions of accuracy, calibration, gas purity, etc., there are several inherent difficulties encountered in endeavoring to measure the ionization per electron per unit path through the gas. The first of these is due to the fact that the electrode system which collects the products of ionization is subject also to charge arising from photo-electric action on the electrodes by radiation excited by electron impacts in the gas. The second difficulty is due to the necessity of apply-

<sup>4</sup> Langmuir, *General Electric Review*, **26**, 731 (1924); Langmuir and Mott-Smith *ibid.* **27**, pp. 444, 538 (1924).

<sup>5</sup> Lenard, *Ann. der Phys.* **12**, 474 (1903); **15**, 485 (1904).

<sup>6</sup> Kossel, *Ann. der Phys.* **37**, 393 (1912).

<sup>7</sup> Mayer, *Ann. der Phys.* **45**, 1 (1914).

<sup>8</sup> Hughes and Klein, *Phys. Rev.* **23**, pp. 111, 450 (1924).

ing a field in the region between the collecting electrodes in order to draw to them the products of ionization and to prevent any of the primary ionizing electrons from reaching these electrodes. Because of this field, the primary electrons do not pass through the gas with a constant speed, but with speeds which vary from that with which they are projected into the ionizing region down to much smaller values (down to zero in the experiments of Hughes and Klein). It is, therefore, impossible to say to just what energy of impact the observed ionization should be ascribed, and it is necessary to compute the desired result by setting up an integral equation to represent the observations and to solve it by differentiating the experimental curve. To the above difficulties might be added a third source of error which arises from any ionization of a cumulative type or from more than one impact by the same primary electron.

In the present work we have eliminated the first and third of these difficulties and reduced the second so that the value for the ionization per electron per centimeter path is set experimentally within rather narrow limits and may be computed within these limits with but a small probable error.

#### APPARATUS AND ITS USE

The apparatus employed is shown in Fig. 1. The filament  $F$  consisted of a few turns of 10 mil (.25 mm) molybdenum wire, in front of which was placed a focusing ring connected to the negative terminal. The narrow tube  $T$  through the bottom of the shielding box served to direct a narrow beam of electrons into the middle region of the chamber  $B$ . The positive ions formed in  $B$  were attracted to the collector  $C$ , which consisted of five 20 mil wires supported at each end by a ring of the same sized wire. The use of small wires for collecting the positive ions had the triple advantage of reducing to an inappreciable value the photo-electric current from this electrode, of reducing the chance that primary electrons which might be scattered in the gas would reach this electrode, and of reducing the effect on the velocity of the primary electrons due to the collecting field  $V_r$ . The ion trap  $S$  served to catch the electrons after passing through  $B$ , and also any positive ions produced after passing through the gauze at the bottom of  $B$ . The chamber  $B$  was 2.8 cm long and about 3 cm in diameter. All metal parts were made of nickel except the filament, and were freed from gas by heating in vacuo to a red heat by high frequency induction currents.

The electrical connections used in making the measurements are shown in Fig. 2. The variable accelerating voltage was measured by a voltmeter  $V_a$ , while  $G_-$  and  $G_+$  measured, respectively, the electron

current  $I_-$  into the chamber  $B$  and the positive ion current  $I_+$  resulting from ionization by the electrons passing through the gas in this chamber. We thought, when beginning the investigation, that a magnetic field produced by a current through a coil wound around the glass jacket and

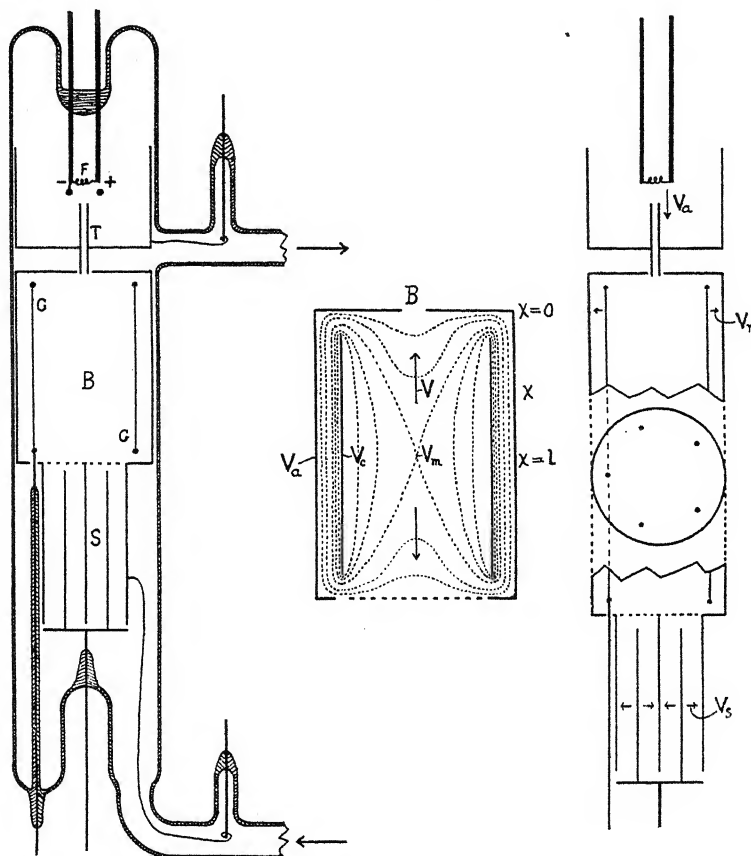


Fig. 1. Electrons from the filament  $F$  were projected through the tube  $T$  into the ionization chamber  $B$  in which the products of ionization were collected by a "squirrel cage" arrangement of wires  $C$ . The non-colliding electrons passed into the ion trap  $S$ . The dotted curves represent equipotential surfaces, with an axial point of minimum potential  $V_m$ , when the potentials of  $B$  and  $C$  are  $V_a$  and  $V_c$ , respectively, with respect to the filament.

coaxial with the chamber  $B$  would prevent electrons from reaching the collector  $C$  and thus permit us to use so small a collecting field as not appreciably to affect the speed of the primary electrons passing through the chamber. When this plan was tried, however, it was found that the ratio of  $I_+$  to  $I_-$  for any given pressure was very irregular, being subject to small variations in the magnetic field, and that these irregularities

could be shifted from lower to higher voltages by increasing the magnetic field. Not succeeding in explaining or eliminating this effect of the magnetic field, we abandoned its use and applied a retarding voltage  $V_r$  to the collector  $C$  to prevent electrons from reaching it. A galvanometer with a sensitivity of about 300 megohms was used as  $G_-$ , while for  $G_+$  were employed a galvanometer of about 11000 megohms sensitivity for the higher currents and a Compton electrometer with suitable India ink shunts for the lower currents.

The gas pressures used were between 0.001 and 0.005 mm mercury in order that the chance of an electron's making more than one collision with gas molecules while passing through chamber  $B$  would be extremely small. It was, therefore, unnecessary to take account of any ionization due to multiple collisions. These pressures were measured by means of a McLeod gauge with a rather fine capillary on the gauge reservoir, and instead of using a capillary of the same size for the outside mercury level,

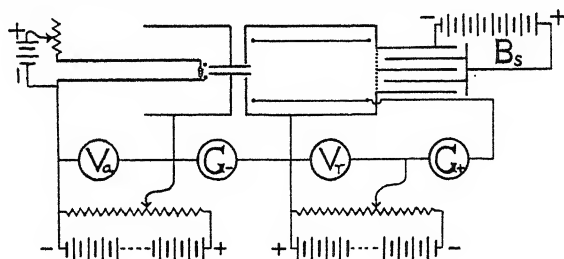


Fig. 2. Circuits. Voltmeters  $V_a$  and  $V_r$  measured the accelerating and collecting fields, and galvanometers  $G_-$  and  $G_+$  measured the total electron current entering  $B$  and the positive ion current due to ionization, respectively.

a 1 cm tube was used. To determine the zero level of the mercury in the 1 cm tube, the capillary depression in a clicking vacuum was determined at various points along the capillary and was found to be everywhere almost exactly 12 mm. So, when a reading was taken, the outside level of the mercury was set 12 mm above the top of the capillary and the pressure read off the calibration curve as usual. The capillary tube was always tapped with a pencil while the mercury was coming to equilibrium in the tubes, to avoid any error due to the adhesion of the mercury to the walls. Also, parallax was avoided by observing the level of the mercury in the capillary through a lens mounted at the end of one edge of a small square. With these refinements the readings of the pressures varied less than 1 percent for different settings on the same pressure. A further check on the accuracy of the pressure readings was made occasionally by finding the product of the length of the gas-filled capillary times the difference in level of the mercury columns (the 12 mm capillary depression being de-

ducted of course) for different levels of the mercury in the capillary. This check was used whenever there seemed to be any pronounced sticking of the mercury in the capillary near the level used in the regular method of reading.

*Determination of gas temperature.* Since the chamber *B* became warm a short time after the filament current was turned on, it was necessary to find the actual temperature of the gas in order to know its density and to be able to reduce the results to standard conditions. Rather than reconstruct the apparatus with a thermocouple attached to *B*, we used the

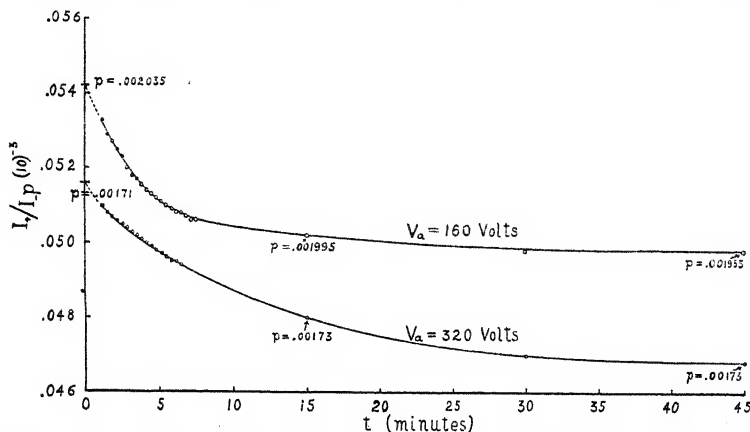


Fig. 3. Typical curves from which was found the temperature of the gas in the ionization chamber *B*. Time was measured from the instant of turning on the filament heating current. The decrease in ordinate (ionization per electron per 0.001 mm gas pressure) was due to the subsequent warming up of the gas. By use as an ionization gauge, the ratio of initial to final equilibrium temperature was computed.

apparatus as an ionization gauge to find the decrease in gas density due to increase in temperature just after the current through the filament was turned on. The positive ion current and electron current were measured at twenty second intervals for at least five minutes, beginning about one minute after the filament current had been turned on, and then at less frequent intervals until stable conditions were reached. Fig. 3 shows the results of two typical runs in mercury vapor, one with  $V_a = 160$  volts and the other with  $V_a = 320$  volts. The ordinates are numbers of positive ions produced per electron in traversing the length of *B*, per 0.001 mm pressure of the vapor.<sup>9</sup> The values of this number at time 0, i.e., at room temperature, are obtained by a short extrapolation of the curves back-

<sup>9</sup> The difference in the shape of these curves is due, for the most part, to the differences in initial pressures and in changes of pressure during the runs. That is the reason for giving the pressures in the figure.



ward. Thus with  $V_a=160$  volts the final ordinate is 91.9 percent of the initial one, and corresponds to a temperature rise of  $26^\circ$  above the room temperature of  $25^\circ$ ; and with  $V_a=320$  volts the final ordinate is 90.7 percent of the initial one and corresponds to a temperature rise of  $30^\circ$  above the room temperature of  $23^\circ$ . From the consideration of nine such runs, it was decided that  $51^\circ\text{C}$  best represents the temperature of the gas in chamber *B* throughout the various observations. The possible variations from this temperature would not introduce any appreciable error.

*Methods of handling the gases.* The hydrogen was prepared by electrolysis of dilute sulfuric acid and was purified by passing over phosphorous pentoxide and through charcoal immersed in liquid air. It was admitted to the experimental tube through a trap immersed in liquid air, and there was also a liquid air trap between the experimental tube and the McLeod gauge and diffusion pump connections. Owing to the very rapid "clean up" of the hydrogen, a reservoir of about 5 liters capacity was attached to the tube to reduce the rate of change of pressure. The pressure was measured at about ten minute intervals during the runs, and the time of each current reading was noted, so that the proper pressure could be used for each individual calculation of the ionization per electron per unit pressure.

The argon was purified by prolonged arcing between calcium electrodes and was admitted to the experimental tube through a liquid air trap. To insure the purity of the neon and the helium in the tube, a charcoal trap, a tube containing copper and copper oxide, and a high pressure diffusion pump were added to the system in such a way that the gas could be circulated by the pump through the glowing copper and copper oxide and the charcoal, which was immersed in liquid air. This circulation was not continued while observations were being made, since the action of the circulating pump caused somewhat erratic variations in the gas pressure within the experimental tube. The helium and neon were each spectroscopically free from each other before being admitted to the system.

The nitrogen first used was generated by the reaction of sodium nitrite and ammonium chloride, stored in contact with phosphorous pentoxide and admitted through a tube immersed in liquid air. After finding that some ionization set in at about 10 volts (see Fig. 5) it was thought that possibly there might be some nitrogen oxides present, so that other runs were made using nitrogen generated by the action of bromine on ammonia and stored over phosphorous pentoxide—a method which is supposed to yield very pure nitrogen.<sup>10</sup> However, the experimental results with the gas prepared by the two methods were almost identical.

<sup>10</sup> Waran, Phil. Mag. 42, 246 (1921).



While making the observations on mercury vapor, the liquid air was removed and the pressure varied for different runs by varying the room temperature. The slight temperature changes during a run were taken account of by noting at ten minute intervals the temperature of a thermometer placed in the vicinity of the system, and the time of each current measurement was noted, as in the case of hydrogen.

For the observations on hydrogen chloride, the gas was generated by the action of sulfuric acid on hydrochloric acid, passed through a sulfuric acid wash bottle, over phosphorous pentoxide and solidified in a tube immersed in liquid air. Then any uncondensed gas was pumped off, and the condensed material was allowed to evaporate into the 5 liter reservoir, after which it was recondensed and the residue again pumped off. This process was repeated until no uncondensable gas remained. The gas pressure in the 5 liter reservoir was then adjusted so that the rate of flow into the experimental system through a fine capillary leak would give a suitable pressure in the experimental tube when the diffusion pump was running. In this way there was no opportunity for the accumulation of products of slow reaction of the HCl vapor on the metallic electrodes. Due care was taken in the arrangement of the McLeod gauge and pump connections so that the gauge would give the true pressure in the experimental tube. Since liquid air temperature is too low to give a suitable vapor pressure of hydrogen chloride, a temperature between  $10^{\circ}$  and  $25^{\circ}$  higher than liquid air temperature was maintained in the traps for keeping out mercury vapor, by surrounding the traps with cylinders of brass closed at the bottom, these in turn being surrounded by large glass test tubes immersed in liquid air. By allowing about an inch of the brass cylinder to extend above the top of the liquid air flask, the pressure of the hydrogen chloride could be made as high as about 0.015 mm. Since there was usually a slight pressure change during a run, the same method of obtaining the correct pressure for each observation was used as in the cases of hydrogen and mercury vapor.

*Potential at the center of chamber B.* In order to prevent any appreciable number of electrons from striking the positive ion collector,  $V_r$  had to be made slightly larger than  $V_a$ . Thus the space through which the electrons passed within the chamber *B* was not field free, but had a potential distribution, probably such as shown in the central part of Fig. 1. The potential with respect to the filament would be a minimum at the center of *B*. Thus an electron, entering *B* with the speed corresponding to  $V_a$ , would be retarded until it reached the center, and then would be accelerated so that it would pass out of *B* with the same speed as that with which it entered, provided it suffered no inelastic collision on the way. Two

methods were used in determining the potential at the center of  $B$ . The first consisted in measuring the total electron current  $I_-$  while  $V_a$  was kept constant and  $V_r$  varied, for a series of values of  $V_a$  both in a vacuum and in hydrogen. When  $I_-$  was plotted against  $V_r$ , a marked change in slope was found in every curve at a value of  $V_r$  about 2.5 times that of  $V_a$ . This critical value of  $V_r$  was interpreted as being the one above which electrons were turned back before reaching the center of  $B$ , some striking the tube  $T$  or the under side of the shield containing it. Therefore  $V_m$ , the potential at the center of  $B$ , may be taken as  $V_a - 0.4 |V_r|$ , where  $|V_r|$  represents the numerical value of the retarding potential applied between  $B$  and  $C$ .

The second method of determining  $V_m$  was to place a sensitive galvanometer in series with the 22.5 volt battery  $B$  (Fig. 2), connecting the two sets of vanes of the ion trap, and noting at what value of  $V_a$ , for a given  $V_r$ , electrons began getting through  $B$  into the ion trap. It was found that they began to get through when  $V_a$  was from 0.40 to 0.45 times  $|V_r|$ , thus confirming the conclusion that  $V_m = V_a - 0.4 |V_r|$ , to a close approximation.

*Methods of measurement and calculation.* Series of measurements were made on all the gases investigated by noting  $G_-$  and  $G_+$  as  $V_a$  was varied from below the minimum ionizing potential to about 320 volts (410 volts in the case of neon to make sure that the voltage for maximum  $I_+$  had been passed) with  $|V_r|$  always about 1.5 volts greater than  $V_a$ . Readings were taken at intervals of one volt to above twice the ionizing potential; then of two volts to about 100 volts; of five volts to about 180, and then of ten volts over the rest of the range. Preliminary tests showed that the ratio  $I_+/I_-$  was independent of the filament temperature, i.e., of  $I_-$ , over a wide range. For convenience, about the same filament current was used all through the investigation and the galvanometers were calibrated at the beginning and end of each individual run. Several runs were made at somewhat different pressures with each gas. The only limitations in the pressures and currents which could be used were (1) that these must be large enough to give sufficient ionization for accurate measurement, and (2) that they must not be so large as to allow appreciable ionization by cumulative action or by more than one impact by an electron.

From the readings of  $G_-$  and  $G_+$ , the galvanometer and electrometer calibrations and the gas pressures, the ratio  $I_+/(I_-p)$ , where  $p$  is the pressure of the gas in mm of mercury, was calculated. Then from the results of three or more such runs which agreed within 2 percent with one another over most of the range for each gas, the mean values of this ratio were found for each voltage  $V_a$ . When these mean values were plotted

against the values of  $V_a$  they gave such curves as curve *a* in Figs. 4 and 5. The ordinates of this curve should give the average number of ionizing collisions made per electron while moving a distance equal to the length of *B* (2.8 cm) through the gas at 1 mm pressure with velocity corresponding to  $V_a$ , if it were not for the fact that the space within *B* is not field free and consequently the electrons do not all have the velocity  $V_a$  when they strike the gas molecules. Two methods were used to take into account this uncertainty, (1) by calculation based on the distribution of potential within *B*, and (2) a direct method whereby the desired quantity can be set by experiment between narrow limits.

*First method.* Of several assumptions made regarding the variation of potential along the path of the electrons in *B*, the one which gave the most reasonable results was the assumption that the potential varies at a uniform rate from the end to the center. Then the value of the potential  $V$  (with respect to the filament) at any point  $x$  in *B* is given by

$$V = V_a - \int_x^l E dx = V_a - E(l-x),$$

where  $l$  is the distance from the center to the end of *B*,  $x$  is the distance of the point  $x$  from the center of *B* and  $E$  is the electric intensity (supposed constant). At the center,  $x=0$ , hence

$$V_m = V_a - El = V_a - 0.4(V_a - V_c)$$

where  $V_c = V_a - |V_r|$  is the potential of the collecting electrode. Thus  $E = 0.4(V_a - V_c)/l$ . Substituting this above, and remembering that  $V_c$  in our experiments was only 1.5 volts, we have approximately

$$V = V_a(0.6 + 0.4x/l). \quad (1)$$

Let  $M = I_+/(I_-p)$  stand for the observed ionization per electron per unit pressure in the chamber *B*. Let  $f(V)$  be the average number of ionizing collisions made by an electron if it passed through *B* with uniform velocity of  $V$  volts, at unit pressure. Then we should have

$$M = \int_{V_m}^{V_a} f(V) d(x/l).$$

Since  $V_m = 0.6V_a$ , and differentiation of Eq. (1) gives  $d(x/l) = (2.5/V_a)dV$ , we have

$$M = (2.5/V_a) \int_{0.6V_a}^{V_a} f(V) dV.$$

By differentiation,

$$0.4 d(MV_a)/dV_a = f(V_a) - f(0.6V_a). \quad (2)$$

In applying this equation to determine  $f(V_a)$  from the experimental values of  $V_a$  and  $M$ , we have two cases to consider:

If  $V_a < 1.67$  times the minimum ionizing potential  $V_i$ , then  $f(0.6 V_a) = 0$ , and we have

$$f(V_a) = 0.4 d(MV_a)/dV_a. \quad (3)$$

If  $V_a > 1.67 V_i$ , then

$$f(V_a) = 0.4 d(MV_a)/dV_a + f(0.6 V_a). \quad (4)$$

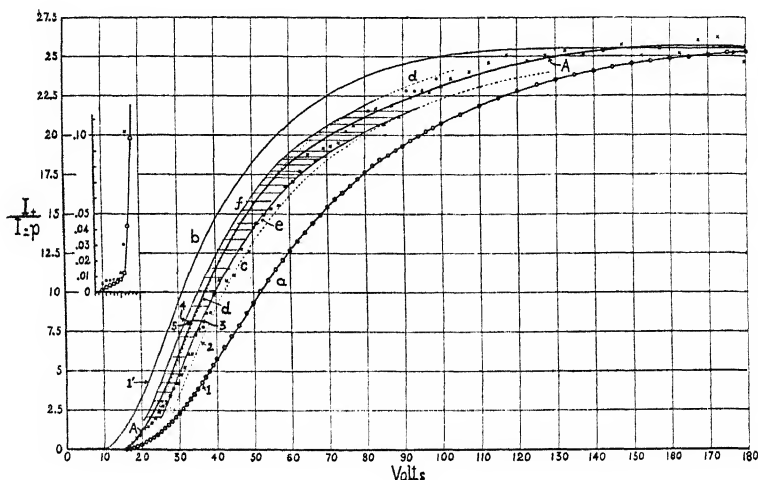


Fig. 4. Curves for nitrogen; positive ions formed per electron per mm pressure per 2.8 cm path as a function of energy of electrons, in volts. Curve *a* gives experimental results when  $V_r = V_a + 1.5$  volts, thus with primary electrons prevented from reaching *C*. Curve *b* gives the same values plotted against the minimum energy  $V_m$  instead of the maximum energy  $V_a$ . The true curve lies between these. Curve *c* gives experimental values when  $V_r$  was adjusted for maximum ionization, and curve *d* gives the same for minimum voltage  $V_m$ . Curves *e* and *f* were obtained by correcting *c* and *d* for stray electron current. The true curve lies between *e* and *f* and is taken as curve *A*. Crosses are points which were computed from curve *a* by method (1).

The values of  $f(V_a)$  were calculated for the different voltages used, by means of Eq. (3) and (4) and plotted at the mid-points  $V_a - \frac{1}{2} dV_a$ , giving results such as are shown by the crosses in Figs. 4 and 5. A rather marked change in slope was noted in all of the  $M$  curves at a value of  $V_a$  approximately twice the ionizing potential, and this break was still more pronounced in the  $f(V_a)$  curves. It was at first suspected that these breaks might be due to ionization of highly excited molecules, or by the double ionization which might occur if a molecule, excited by an energy at least twice the minimum ionizing energy, should make a collision of the second kind with a neutral molecule. Such effects should, however, tend

to disappear at very low gas pressures, whereas we found that the curves, including this break, were identical down to extremely low pressures. In the second method, described below, it was found that this break shifted according to the value of  $V_r$ , so that we are inclined to attribute it to a peculiarity of the field within  $B$ , due to lack of radial symmetry of the collecting electrode system. It probably indicates a second order error in the values of  $M$  and  $f(V_a)$  in the lower voltage ranges.

*The second method* for finding the number of ionizing collisions which would be made by an electron moving with a uniform speed  $V_a$  through  $B$  in gas at unit pressure, can be best explained by referring to Fig. 4. Consider, for instance, the experimental reading marked 1. Here the electrons entered the chamber  $B$  with velocity of 36 volts and reached the center of  $B$  with velocity of 0.6 of 36, or 24 volts. The ordinate at 1 must therefore be the value of  $f(V_a)$  corresponding to some value of  $V_a$  between 36 and 24 volts. In other words, the corresponding point on the  $f(V_a)$  curve must be somewhere between 1 and 1'. Similarly for every point on curve  $a$  there is a corresponding point on curve  $b$  which is shifted to the left by an amount 0.4 of  $V_a$ . The true curve for  $f(V_a)$  must lie between the curves  $a$  and  $b$ .

Now, by decreasing the field  $V_r$  to a value considerably less than  $V_a$ , keeping  $V_a$  constant at 36 volts, it was found that the current  $I_+$  increased to a maximum value when  $V_r$  was 11 volts, and then decreased with further decrease in  $V_r$ . The reason for this is that decrease in  $V_r$  produced two opposing effects: (1) It diminished the retardation of the electrons, thus causing them to traverse  $B$  with speeds more nearly equal to  $V_a$ , and thus increased the ionization produced by them; (2) it permitted some electrons to reach the collecting electrode, and thus diminished the apparent amount of ionization. The observed value of  $I_+$  corresponds to point 2 in Fig. 4. Owing to the electrons which reached the collecting electrode, the true ionization must have been somewhat greater than this. The amount by which it was greater was determined by making a similar measurement with the gas removed from the tube, so that the stray electron current only was measured, and this was checked by similar measurements in the gas at values of  $V_a$  less than  $V_i$ . Adding this to the current corresponding to point 2 gives the current which would have been observed with  $V_r$  equal to 11 volts, had there been no reverse current due to electrons. This ordinate at point 3 corresponds to electrons which entered  $B$  with velocity 36 volts, and whose velocity fell by 0.4 of 11 volts, or by 4.4 volts within  $B$ . Thus the ordinate is the value of  $f(V_a)$  for some value of  $V_a$  between 36 and 31.6 volts. Thus the limits within which the value of  $f(V_a)$  must lie have been much narrowed down; it must lie be-

tween points 3 and 4. A consideration of all the factors involved led to the choice of point 5 as the most probable point, and it is certain that this value of  $V_a$  and  $f(V_a)$  cannot be in error by more than a few percent. In this way, the values of  $f(V_a)$  were found and plotted as curve *A*, which lies between the experimentally fixed limits shown by curves *e* and *f*.

Of the two methods, the second is the more reliable in that it does not depend on any assumption regarding the distribution of potential within *B*. The agreement between the two methods is indicated by the way in which the crosses are distributed with respect to the experimental limits

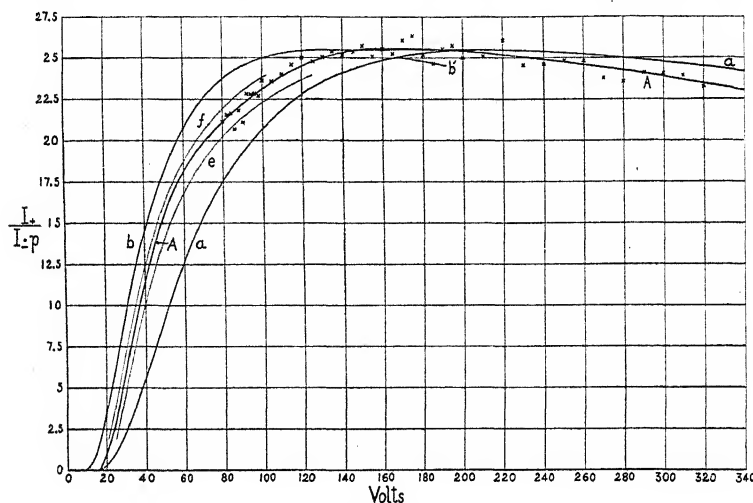


Fig. 5. Extension of Fig. 4 to 340 volts.

shown by the shaded region between curves *e* and *f*. The agreement is best at the higher voltages, where the variation of  $f(V_a)$  with  $V_a$  is less rapid. Curve *A* has been drawn with reference to the second method at the lower voltages, and with reference to the first method at the higher voltages, where the two methods converge to give the same results. Curve *A* gives, for nitrogen, the average number of ionizing collisions which would be made by an electron moving with constant speed  $V_a$  through chamber *B* containing the gas at 1 mm pressure. Fig. 5 shows the same results, continued to the higher voltage ranges.

#### DISCUSSION OF RESULTS

If the values of the ordinates of curve *A* are divided by the length of the chamber *B*, they give the average number  $N$  of ionizing collisions per electron per cm path per mm gas pressure as a function of the velocity. The assembled results of our experiments are shown in Fig. 6, where  $N$



stands for the quantity defined just above. It is of interest to note that the value of  $N$  continues to decrease with still greater electron speeds. For air, according to Kossel<sup>6</sup>  $N$  decreases from about 10 at 200 volts to 3.3 at 1000 volts, 0.4 at 30,000 volts and 0.18 for  $\beta$ -rays.

The probability  $P$  of ionization at an impact may be found by dividing these values of  $N$  by the number of collisions per cm path made by an

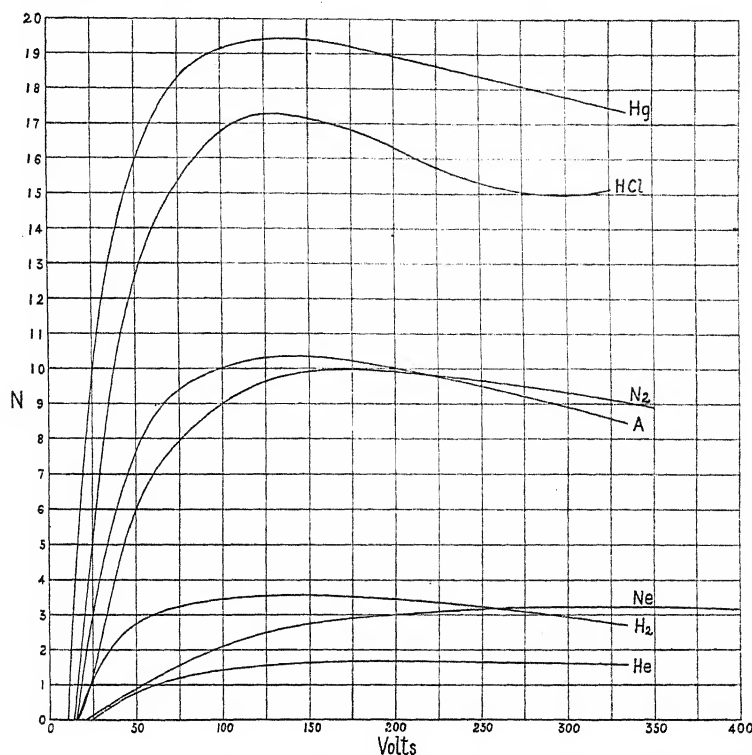


Fig. 6. Number of positive ions formed per electron per cm path through gas at 1 mm pressure, as a function of the electron energy in volts.

electron moving through the gas at 1 mm pressure. Although there is some uncertainty regarding the true values of this number, the experiments of Ramsauer<sup>11</sup> and Mayer<sup>12</sup> indicate that the ordinary kinetic theory value of electronic mean free path is at least approximately correct at speeds as large as those in which we are interested, except for argon at the lower speeds. We shall, therefore, assume that the electronic mean free path equals  $4\sqrt{2}$  times that of the gas molecules. The values are given

<sup>11</sup> Ramsauer, *Ann. der Phys.* **64**, 513 (1921); **66**, 546 (1921).

<sup>12</sup> Mayer, *Ann. der Phys.* **64**, 451 (1921).



in Table I. They are calculated from values given in "High Vacua," by Dushman, except in two cases for which the data were not available there and were obtained from Kaye and Laby's Tables. All are calculated for a temperature of 25°C. The values of the probability  $P$  are shown in Fig. 7.

TABLE I

Gas:	He	Ne	A	H <sub>2</sub>	N <sub>2</sub>	Hg	HCl
$l$ :	0.1259	0.0787	0.0451	0.0817	0.0425	0.0149	0.0322
$1/l$ :	7.95	12.80	22.18	12.24	23.52	66.70	31.05

A comparison of our results with those of Hughes and Klein, while showing agreement as to general features and orders of magnitude, brings out discrepancies which are difficult to explain. The fact that

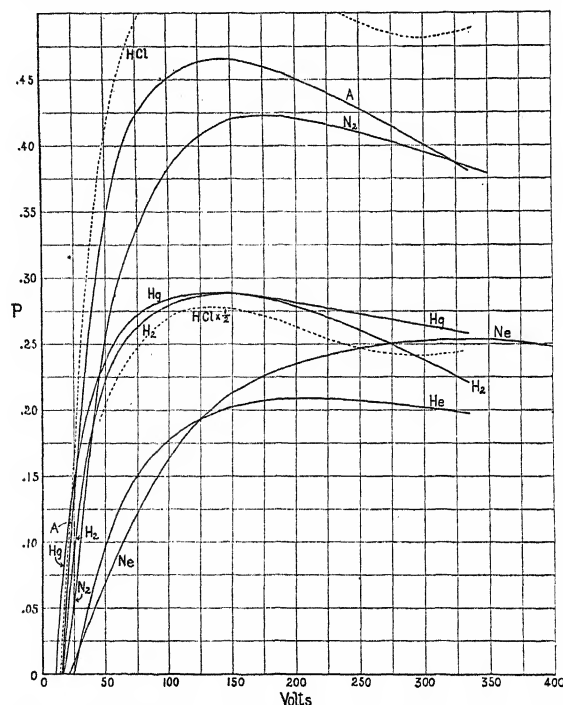


Fig. 7. Probability of ionization at an impact as a function of the electron energy in volts, assuming kinetic theory values of electronic mean free paths.

their values are consistently smaller than ours may be due to the fact that they appear not to have taken account of the heating of the gas in the apparatus by the filament. We feel that their results are definitely too low, since they fall below the lower limit set by curves, such as curve  $e$  of Figs. 4 and 5, which are the direct result of measurement and depend on no calculations or assumptions, but only on the calibration of the gal-

vanometers and the McLeod gauge. Some aspects of this comparison are shown in Table II. This table also contains values from a recent paper by Jesse.<sup>13</sup> Although he does not claim much accuracy for his absolute values of  $N$ , his results agree more closely with ours than do those of Hughes and Klein.

TABLE II

Gas	$N(\text{max})$			$V_a(\text{max})$		
	(authors)	(H. & K.)	(Jesse)	(authors)	(H. & K.)	(Jesse)
He	1.65	0.881	1.61	210	150	140
Ne	3.22	1.828	3.16	340	160	220
A	10.33	7.65	14.5	140	80	100
H <sub>2</sub>	3.55	2.518	.....	145	73.5	...
N <sub>2</sub>	9.96	7.640	10.3	175	100	100
Hg	19.44	.....	.....	135	.....	...
HCl	17.30	.....	.....	130	.....	...
CO	.....	.....	12.8	...	.....	120
CH <sub>4</sub>	.....	8.06	.....	...	80	...

Mention should also be made of a recent paper by Gladys A. Anslow<sup>14</sup> on "Total Ionization Produced in Air by Electrons of Various Energies," in which conclusions are reached with regard to the ionization per electron per cm path at 1 mm pressure which differ very markedly from the conclusions of the present paper, both in magnitude and in the nature of the dependence upon electron speed. In considering Miss Anslow's work, it should be noted that the gas pressures at which her observations were taken were determined by extrapolation of a certain curve which was interpreted as giving the "critical pressure" at which the electrons just failed to reach the walls of the ionization chamber before having completed their total ionization, so that it was assumed that all electrons lost their ionizing energy by collisions with gas molecules before escaping from the chamber. This cannot have been true, however, as a simple calculation based on electron mean free paths shows. For all of her voltages below 1000 volts, an appreciable number of electrons would have traversed the ionization chamber without having collided at all; below 300 volts the majority would have thus escaped collision, while at the maximum of her curve, Fig. 6, not more than one percent of the electrons would have collided. Thus the interpretation of the results at the lower voltages is incorrect and these results cannot be taken as inconsistent with the results of the present paper. Incidentally, we believe that the maximum in Miss Anslow's Fig. 6 is due to the combination of the variation in the number of electrons which collide and the variation of the probabilities of ionization at the different pressures and voltages used.

<sup>13</sup> W. P. Jesse, *Phys. Rev.* **26**, 208 (August, 1925).

<sup>14</sup> Gladys A. Anslow, *Phys. Rev.* **25**, 484 (1925).

On the basis of measurements with the ionization gauge, Dushman<sup>15</sup> suggested that the ionization in different gases is proportional to the total number of electrons in the molecules of the gases. The present results do not support this suggestion as a quantitative relation. It may be, however, that the proposed relation is more accurate at higher voltages than those at which we worked—as might be expected on theoretical grounds and as is indicated by the early work of Kossel,<sup>16</sup> who made the same suggestion on the basis of measurements at 1000 volts.

Finally, the apparent ionization of nitrogen at about 10 volts (see Fig. 4) raises an interesting question of interpretation. As shown in the insert, this is extremely weak as compared with the ionization setting in at the ordinary ionizing potential. Three possibilities present themselves: (1) It may represent a weak and hitherto undiscovered type of ionization of nitrogen; (2) it may be due to photo-electric effect on the collecting electrode *C* by radiation excited in the gas; (3) it may be due to electron emission from the collecting electrode *C* produced by contact with "excited" or "active" molecules of nitrogen. In opposition to the second suggestion is the fact that in no other gas was there any detectable current which could be ascribed to photo-electric effect; the scheme for eliminating complications from this cause seemed to be quite successful. In favor of the third suggestion is the fact that this observed critical potential agrees well with the internal energy of at least one type of active nitrogen, which has been placed at 9.52 volts by Saha and Sur,<sup>16</sup> as revised by Foote, Ruark, and Chenault.<sup>17</sup> If this is the correct interpretation, the detection of the active nitrogen by an apparatus relatively insensitive to the photo-electric effects would be due to the greater probability of electron emission at a collision of the second kind between an excited molecule and the metal than by photo-electric action of radiation. If this be true, it must still be remarked that the efficiency of these low voltage impacts in producing active nitrogen must be quite small, else Duffendack would have detected it in his low-voltage arcs.<sup>18</sup> We hope later to be able to give a definite answer to this question.

*Note added with proof.* Further consideration of the work by Hughes and Klein<sup>8</sup> and by Jesse<sup>13</sup> indicates that in both cases the assumed values of primary electron current must be in error. The former are too large, owing to an incorrectly assumed linear relation between current and field on one side of the grid. The latter are too small on account of neglect of

<sup>15</sup> Dushman, "High Vacua"; Dushman and Found, *Phys. Rev.* **23**, 734 (1924).

<sup>16</sup> Saha and Sur, *Phil. Mag.* **48**, 421 (1924).

<sup>17</sup> Foote, Ruark, and Chenault, *Phys. Rev.* **25**, 241 (1925).

<sup>18</sup> Duffendack, *Phys. Rev.* **20**, 665 (1922).

secondary electrons which subtract from the primary electron current. Experiments are being undertaken to see whether these corrections are adequate to account for the discrepancies in the three experiments on this subject. It may be noted that in the present work both the ionization and the primary electron currents were measured directly, and that secondary electrons were avoided by use of the electron trap.

PALMER PHYSICAL LABORATORY,  
PRINCETON, NEW JERSEY,  
July 16, 1925

## POST-ARC CONDUCTIVITY AND METASTABLE HELIUM

BY CARL ECKART

## ABSTRACT

Conductivity of helium immediately after arcing through it.—A study has been made of the abnormal conductivity which Kannenstine found persisted for .007 sec. after the arc was extinguished. The results prove that the residual conductivity is due to positive ions and not to metastable excited helium atoms, as suggested by Kannenstine. By means of adjustable commutators, the arc tube was connected first to a battery which caused an intense arc (period A), then after a brief interval (period B) to a source of voltage  $V_c$  through a micro-ammeter (period C). As  $V_c$  was increased the micro-ammeter showed a small negative current (positive ion) to 1.2 v., then a regularly increasing positive current reaching saturation at 8 v. The logarithm of the saturation current was a linear function of the length of period B for  $V_c = -15$  v. and for  $V_c = -26$  v., the current decreasing to one tenth in from .004 to .007 sec. (*Similar observations in mercury* gave a constant of .01 to .02 sec.). Observations with a Braun tube oscillograph gave direct additional evidence that after the arc ceased, the current decreased exponentially with time, independent of the length of the interval B. An attempt to sweep the positive ions away by applying a high negative voltage during B failed. Spectrographic observations made with a rotating slit attached to the commutator showed that no light was emitted during period C, even when the helium had been so carefully purified that the bands were distinctly visible in the spectrum of the arc.

Life of metastable helium (states 2S and 2s).—While there is good evidence that metastable helium atoms persist for a longer time than ordinary excited atoms, the only evidence for a life of the order of 1/140 sec. rests on Kannenstine's interpretation of the persistent post-arc conductivity, and the experiments in this paper prove his interpretation to be unjustified.

## INTRODUCTION

SOME of the most interesting developments in the study of the atom, center about the so-called metastable states. The valence electron of an atom in such a state moves in an orbit whose energy is greater than that of the normal orbit, but a reversion from this orbit to the normal with the emission of radiation is forbidden by the selection principles. The length of time that the atom persists in a metastable state will presumably be longer than for the ordinary excited state, for the ordinary excited state is terminated by the emission of a quantum of radiation, a process which is usually determined primarily by the internal mechanics of the atom. The energy of the metastable state, however, cannot escape from the atom without the co-operation of some external agent, most likely another atom, and a process involving two atoms is much less probable, other things being equal, than one involving a single atom.

Franck and Reiche<sup>1</sup> used this hypothesis of a long life to explain certain absorption phenomena observed by Paschen in helium. The hypothesis has since been supported by a variety of observations on helium, mercury, and other elements; but estimates of the actual duration of the metastable state are by no means consistent. Indirect evidence points to a life of the order of  $10^{-6}$  or  $10^{-5}$  sec. for metastable helium, while an apparently very direct determination by Kannenstine<sup>2</sup> gave 1/140 sec. In the case of mercury, the lower limit is about the same, and the upper value, due to Marshall,<sup>3</sup> using Kannenstine's method, is 1/22 sec. It is the purpose of this paper to determine whether the larger values given by Kannenstine's method are reliable.

The method employed by Kannenstine was first suggested by Franck and Reiche and is based on the following considerations. If helium is bombarded by 20 volt electrons, a large proportion of the atoms are thrown into the metastable state. The atoms in this state can be ionized by the impact of a 4 volt electron. Consequently, if the potential accelerating the bombarding electrons is suddenly reduced from 20 v. to 4 v., the current flowing should be abnormally high until all the excited atoms are ionized or disappear due to other causes. The duration of this abnormal post-arc conductivity was therefore taken by Kannenstine and Marshall as a measure of the life of the metastable atom.

However, under the conditions of the experiment the concentration of positive ions in the gas is comparable with, if not very much greater than, the concentration of metastable atoms. Further, the life of an ion may be expected to be comparable with the life of a metastable atom. It therefore becomes necessary to show that the abnormal currents are not due to ions formed during the arc period, rather than to ions formed from metastable atoms during the post-arc period.

#### EXPERIMENTAL PROCEDURE AND RESULTS

1. Kannenstine's experiments were repeated, using a more sensitive means of measuring the post-arc conductivity. A commutator<sup>4</sup> was used which connected the arc tube to a source of 30 to 60 volts d.c. for a certain time interval (period A) determined by the speed of the shaft. This caused an intense arc. During a shorter time interval (period B) immediately following, the arc tube was disconnected from any source of current. The length of this period could be varied independently of period

<sup>1</sup> Franck and Reiche, *Zeits. f. Phys.* **1**, 154, 320 (1920).

<sup>2</sup> Kannenstine, *Astrophys. Jour.* **59**, 135 (1924).

<sup>3</sup> Marshall, *Astrophys. Jour.* **60**, 142 (1924).

<sup>4</sup> I wish to thank Professor E. P. Adams for the use of this apparatus.

A. Then, during a third interval (period C), the arc was connected through a micro-ammeter to another source of voltage  $V_c$ . The connections during the three periods are shown in Fig. 1.

The micro-ammeter thus read the time average of a current which was zero except during period C. For some experiments, the micro-ammeter was replaced by a galvanometer.

If the post-arc conductivity is due to the ionization of excited atoms, then for  $V_c$  less than about 4 v. (the ionizing potential of the metastable atom) only the current due to electron emission from the cathode should

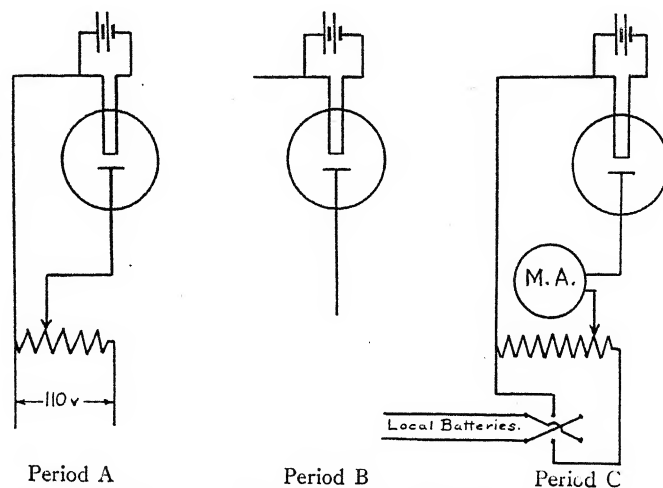


FIG. 1. Connections during each of the three periods.

be observed. At  $V_c=4$ v., the current should begin to rise rapidly, possibly approaching a limit for voltages greater than 4 but less than the first excitation potential of normal helium.

The actual relation between current and voltage during period C is shown in Fig. 2, which is typical of a large number of runs. For voltages less than 1 v., the current was negative, i.e., of opposite sign to any possible thermionic current. It may be remarked immediately that this current was much too large (10 to 50 micro-amp.) to be photoelectric in origin. The only possible explanation is that it was due either to a large supply of positive ions in the tube, or to reactance in the external circuit. As  $V_c$  was increased from 1 to 3.5 v., the current increased very rapidly. Further increase in  $V_c$  produced an additional increase in current, but a saturation value was soon reached. The current then remained constant to within a few percent until the first excitation potential of the normal atom (20 v.) was reached. It is to be noted that the ratio between this saturation current and the positive ion



current is of the order of magnitude of  $\sqrt{M/m}$  where  $m$  is the mass of the electron and  $M$  of the positive helium ion.

In various runs, current readings were taken at small voltage intervals from 1 to 8 v. The results were plotted in various ways which would have accentuated any change in the functional relationship between  $I$  and  $V_c$ . The only changes observed were gradual ones, resembling those found in the current-voltage relationship of the Langmuir exploring electrode<sup>5</sup> much more nearly than those due to critical potentials.

To make certain that no spurious reactance effects were causing these currents, the voltage during period A was reduced from 30 v. to 23 v.,<sup>6</sup> at which value the arc no longer struck. If the currents during C were due to capacitance, they should be reduced in approximately the ratio

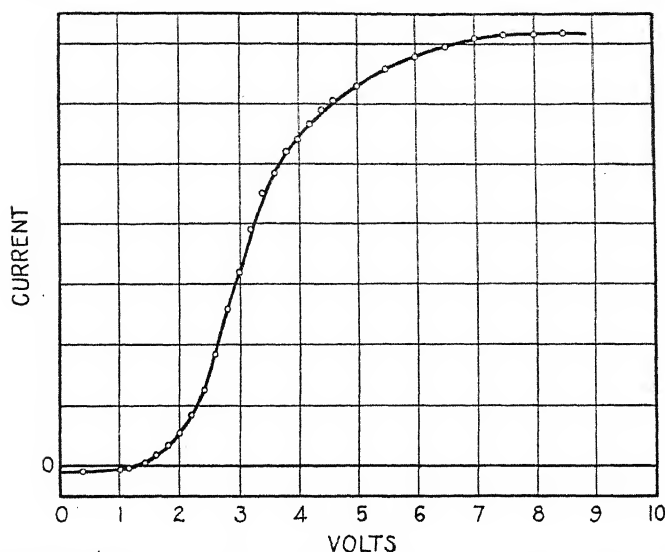


FIG. 2. Relation between current and voltage during period C. Period A = .0045 sec.; period B = .0008 sec.; period C = .0045 sec.

23:30. Actually, under these conditions, only the normal thermionic current could be obtained. Then the arc tube was replaced by a non-inductive resistance, and the voltage during period A adjusted so that the current flowing was about the same as that flowing under the conditions of Fig. 2. The current during period C was now approximately

<sup>5</sup> Langmuir, Gen. Elec. Rev. 26, 713 (1923); Langmuir and Mott-Smith, Gen. Elec. Rev. 27, 444, 538 (1924).

<sup>6</sup> These voltages have not been corrected. They are the readings of a voltmeter which was continuously connected across the potentiometer (Fig. 1). As the arc was connected to the same terminals only during a fraction of the time, the readings are considerably higher than the actual voltage across the arc-tube when it was drawing current.

proportional to  $V_c$  and independent of the speed of the commutator, indicating that inductance effects were negligible.

2. In order to determine the rate of decay of this post-arc conductivity, period B was varied while periods A and C were kept constant. This was possible because the segments of the commutator that made contact during period A were on a separate drum from those that made contact during period C. These two drums could be rotated relative to each

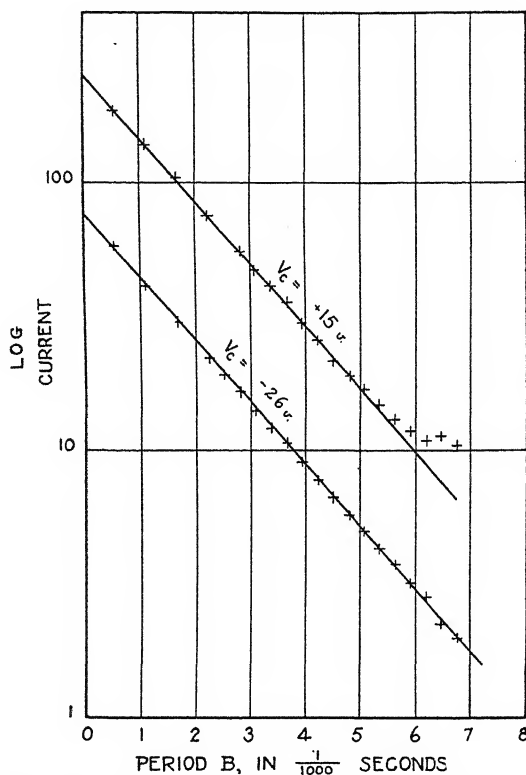


FIG. 3. Variation of average current during period C with the length of period B. Period A=period C=.014 sec. The ordinates of the two graphs are not comparable.

other and then fastened to the shaft with set screws. The angles corresponding to the three periods having been determined, a measurement of the speed of the commutator furnished the remaining datum for calculating their actual lengths in seconds.

For each length of period B, two current readings were taken, one at +8 v. and one at -20 to -30 v. The results of a run of this kind are shown in Fig. 3, where the logarithm of the current is plotted against the length of period B. It is very remarkable that the graphs thus obtained

should be linear, and even more remarkable that the points for positive currents should lie on a line which is almost exactly parallel to the line for the negative currents. This indicates that the positive currents are proportional to the negative currents. So simple a relation would not be expected if the positive currents were determined by an entirely different mechanism from that determining the negative.

Not all of the runs showed this proportionality as distinctly as Fig. 3, but an explanation of this will be given below. However, the negative currents could almost always be represented by an equation of the form

$$I = K (10)^{-t/b} \quad (1)$$

where  $t$  is the length of period B in seconds. For helium, all values of  $b$  which were observed ranged between .004 and .007 sec. If it is assumed that Kannenstine's apparatus could no longer detect the abnormal conductivity after it had fallen to, say, 1/20 of its original value, the agreement with his result of 1/140 sec. is very satisfactory.

Some hasty experiments using mercury instead of helium showed that all phenomena were essentially the same and yielded values for  $b$  of .01 to .02 sec. Marshall's value of 1/22 sec. is again in good agreement.

3. The foregoing experimental method has the advantage of high accuracy, but the disadvantage that it yields only average values of the post-arc conductivity. Kannenstine's use of a Braun tube oscillograph enables instantaneous values of the current to be obtained. Accordingly, a Braun tube was introduced into the circuit so that it indicated the current during all three periods. The spot was given a uniform horizontal motion across the screen by discharging a condenser in synchronism with the commutator through a thermionic valve. The vertical deflection, proportional to current, was obtained either by magnetic or electrostatic deflection. In the latter case, the current was passed through a non-inductive resistance, shunted across the deflector plates.

In Fig. 4 are shown tracings of photographs of the Braun tube figures. The regions corresponding to the three periods are marked. Conditions during periods A and B were not varied, but the voltage across the tube during period C was given the various values indicated. When  $V_c$  was 1 v., the current was too small to be indicated (instantaneous values probably less than 15 micro-amp.). At 1.5 v. the current was still small, but definitely noticeable. As  $V_c$  increased from 1.5 to 3.5 v. (the region of rapid increase of current, Fig. 2) the type of figure did not change. The current rose gradually from zero to a value determined by the voltage, and then remained constant until the end of the period.

At  $V_c = 4$  v., the type of figure began to change. The current rose to a maximum and then diminished again, the shape of the curve suggesting

strongly that it could be represented by an equation of the form

$$I = Ke^{-t/a}(1 - e^{-t/c}). \quad (2)$$

When  $V_c$  was increased beyond 8 v., the shape and size of the figure remained constant.

When the currents were increased by raising the filament temperature, a transition stage (Fig. 5a) became clearly distinguishable. This stage was especially marked when the speed of the commutator was reduced, so that period C was long. The presumption is that stages *bcd* of

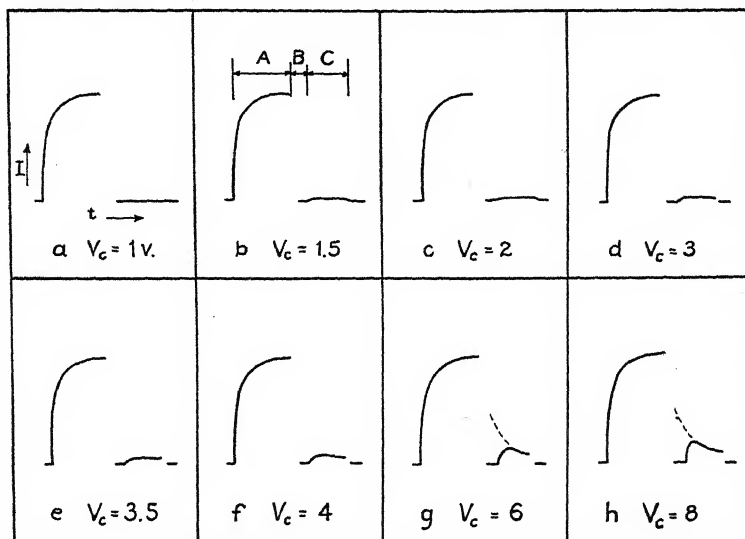


Fig. 4. Tracings of photographs of Braun tube figures.  
Period A = period C = .002 sec.

Fig. 4 are really identical with that of Fig. 5a, but that period C ended before the decrease in current became apparent. Furthermore, under certain conditions it was impossible to pass beyond this stage even when  $V_c$  was made as high as 10 v. The value 4 v. at which the type of figure begins to change in Fig. 4, has thus no significance.

These results show beyond doubt that the post-arc currents are limited by more than one cause. Some indication of the probable character of these causes may be obtained from the two experiments now to be described. In the first the arc tube was replaced by a non-inductive resistance of about 1000 ohms. A voltage was applied through the commutator and the current-time curve obtained with the Braun tube. The current rose to a constant value in what appeared to be an exponential fashion, as was to be expected. The time required for the constant value to be reached was of the same order of magnitude as that

occupied by the convex portion of the curve during period C in Figs. 4 and 5a. The presumption is, therefore, that the factor  $(1 - e^{-t/c})$  in Eq. (2) is introduced by the reactance of the circuit, and is not indicative of any change within the tube.

In the second experiment, the arc-tube was again placed in the circuit, and a photograph of the Braun tube figure taken under the conditions of Fig. 4,(h). Period B was then lengthened considerably, nothing else being changed, and the resulting figure superposed on the previous exposure. A tracing<sup>7</sup> of the plate obtained in this way is shown in Fig. 5b. This result must be interpreted to mean that the convex portions of the curves in Figs. 4 and 5a are determined by phenomena inside the tube, *and that these phenomena are independent of the amount of electricity which has passed through the tube.* In other words, the value of the factor

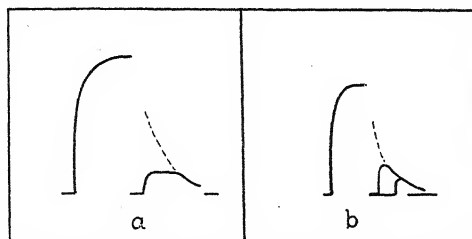


Fig. 5a. Braun tube figure showing transition stage with higher current.

Fig. 5b. Braun tube figures for  $V_c=8$  and for two lengths of period B.

$Ke^{-t/a}$  in Eq. (2) is determined entirely by conditions inside the tube at the end of period A, and not at all by the length of period B. In the method of section 2, this factor is obviously the one which will affect the micro-ammeter reading most strongly. The linearity of the upper graph of Fig. 3 is thus explained, if we assume that the readings were taken under the conditions of Fig. 4 (h). The fact that these graphs were not always linear is explained by Fig. 5a. If the readings for Fig. 3 had been taken under these conditions, no straight line would have been obtained.

No satisfactory explanation has been obtained for the horizontal portion of Fig. 5a, though an interesting hypothesis has suggested itself, which is reserved for further experimental consideration. For the present, it will merely be remarked that Kannenstine and Marshall apparently performed all their work under the conditions of this figure.

Returning to the discussion of Fig. 5b, it must be interpreted to mean that nothing inside the tube is used up by the passage of current during

<sup>7</sup> On the original plate, the lines were very much less definite than in the tracing. There is no doubt, however, that the relation is essentially as drawn in Fig. 5b.

period C. This is not what would be expected if the abnormal conductivity were due to the ionization of metastable atoms. If the large currents are due to the neutralization of negative space charge by positive ions already present, however, this result is quite explicable, for the velocity of the positive ions under such low fields would be very small, and only a very small portion of the total current would be carried by them. Furthermore, there is good experimental evidence that positive ions disappear by recombination with electrons at the walls of the tube and relatively only slowly by recombination in the body of the gas.

Some portions of the theory outlined in this section are possibly more detailed than is justified by the amount of experimental evidence presented and should be considered as merely provisional. It has been shown, however, that the hypothesis that persisting positive ions are the cause of the abnormal post-arc conductivity is better capable of explaining some of the phenomena than is the metastable helium hypothesis of Kannenstine.

4. Several crucial experiments are suggested by the above theory. If the current during period C is determined by positive ions which are in the tube during the entire period B, it is to be expected that the application of a high negative voltage across the electrodes during period B would sweep them out of the tube, and thus materially alter the conductivity during C. Accordingly, a commutator was constructed by means of which it was possible to perform this experiment. The two drums which determined periods A and C each had four contacts. A third drum had only two, shorter contacts. This drum was oriented so that it made contact with its brushes during alternate intervals between A and C. In this way it was possible to obtain simultaneously on the Braun tube screen the figures corresponding to two different sequences of periods: ABC and AB'C. ABC was the sequence previously used (see Fig. 2); AB'C was the same except that during B' the arc-tube was connected to a third source of voltage.

With this apparatus, the experiment of Fig. 5b could be repeated with great ease by merely making the voltage during B' the same as that during C. The comparison of ABC with AB'C was visual and instantaneous. No double photographic exposure was necessary.

When the voltage during B' was made negative, however, it was found that this had little or no effect on the current during C. This was the case, even when a negative voltage of  $-135$  was applied. This result is somewhat disconcerting, but may probably be explained by the shortness of the interval during which the negative voltage could be applied. It is also possible that the potential gradient set up inside the tube was

not as great as would be indicated by the applied voltage. This would be the case if a positive ion sheath were formed over the anode, which Langmuir<sup>5</sup> has shown to be the case when an electrode at a very negative voltage is introduced into a region of intense ionization.

5. A further possibility of distinguishing between the two hypotheses is to be found in the mechanism of the disappearance of positive ions discussed above. If the currents during C are due to the persistence of actual ions, no spectral emission will be expected during this period, even though the current flowing is quite large, but if ionization of excited atoms is the cause of the conductivity, then the spectral emission during C should be comparable to that during A, since the currents flowing are comparable.

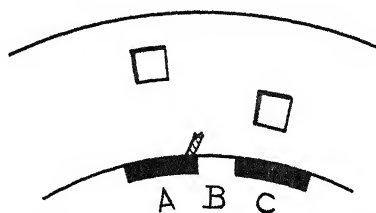


Fig. 6. Diagram showing relative position of perforations in disk and of the commutator segments.

In order to compare the intensity of the spectrum during the two periods, a perforated disk was mounted on the same shaft as the commutator. This is shown diagrammatically in Fig. 6. The disk contained two sets of perforations, and an image of the arc was thrown on it by a large RR objective in such a way that one portion of the image was exposed by one set of perforations during period A, while a symmetrical portion was exposed by the other set during period C. The electrical circuits and the speed of the commutator were then adjusted so that the current during period C was one quarter to one third that during A. Observation showed an intense visible discharge during A but no trace of spectrum during C.

A comparison of the spectral intensities was made with a small Hilger spectrograph. The stronger helium lines were visible on the portion of the plate exposed during period A when the exposure time was three minutes. They were not visible on that part exposed during period C, even when the exposure time was increased to 20 minutes.<sup>8</sup>

<sup>8</sup> It should be noted that these experiments do not indicate that the spectrum disappears instantaneously when the voltage is removed, but merely that it does not persist as long as the post-arc conductivity. What bearing this result has on the work of Webb and (Miss) Hayner (Phys. Rev. 23, 294, 1924; 26, 364, 1925) is not obvious.



6. The helium band spectrum is an excellent indicator of the concentration of metastable atoms built up during the discharge. Consequently, if the post-arc currents are due to metastable atoms, their intensity should vary with the intensity of the band spectrum.

All of the experiments so far described were performed with helium which would ordinarily be called pure, but this helium showed no trace of the band spectrum when the discharge was passed through it at the pressure (3 mm) used. The helium was now treated by a method used by Paschen<sup>9</sup> to remove sub-spectroscopic traces of impurity. A small amount of electrolytic oxygen was admitted into the arc tube containing the helium, and the arc discharge was then allowed to run until the oxygen spectrum was no longer visible. After two such treatments the band spectrum appeared with considerable intensity. The lines were identified with a Hilger direct reading spectrometer. The characteristic yellow band, shading off toward the violet, was distinctly visible. While the helium was in this state of purity a number of the previous experiments were repeated, but no differences in the results could be detected with certainty. In particular, no spectrum was observed during period C under these conditions.

#### CONCLUSIONS

1. The only experimental evidence in favor of a very long life ( $10^{-3}$  to  $10^{-2}$  sec.) of metastable atoms rests on the assumption that the abnormally high conductivity of helium immediately after a discharge has passed through it is due to the presence of metastable atoms.

2. It is shown that the evidence is not in favor of this assumption, but that the abnormal conductivity is due to the persistence of actual positive ions, and accompanying electrons.

3. That the metastable states ( $2S$  and  $2s$ ) in helium have a longer life than other excited states is not questioned by this work but that their life is as long as has been stated by Kannestine ( $1/140$  sec.) is shown to be untrue.

I wish to thank Professor K. T. Compton for his constant and helpful interest in this work, and the Board of Directors of the Edison Lamp Works for their generous support of a fellowship which made the prosecution of this research possible.

PALMER PHYSICAL LABORATORY,  
PRINCETON, NEW JERSEY,  
May 4, 1925

<sup>9</sup> Paschen, *Ann. der Phys.* **45**, 625 (1914).

## THE MOBILITY OF ARGON AND HYDROGEN IONS IN AIR

BY HENRY A. ERIKSON

## ABSTRACT

The apparatus and method are the same as previously used to measure the mobilities of air,  $\text{CO}_2$  and other ions in air, the freshly formed ions being driven across a stream of air by means of an electric field. Two positive ions and one negative ion were found in both argon and hydrogen as in the case of air. The initial positive hydrogen ion was found to transform into the second, and this is doubtless also true in the case of argon, though it was not proved. The mobilities are also the same as obtained for the air ions except in the case of the negative hydrogen ion which has a higher mobility than the negative air ion. It is thus found that the following monomolecular ions all have the same mobility in air at normal pressure: monatomic A, initial + and -; diatomic air, initial + and -; diatomic  $\text{H}_2$ , initial +; triatomic  $\text{CO}_2$ , initial + and -. Thus the mobility of these ions seems to be independent of the masses. The only exception so far found is the negative  $\text{H}_2$  ion.

IN earlier articles<sup>1</sup> are given the results obtained from measurements of the mobility of ions of air,  $\text{CO}_2$  and actinium active deposit in air. In the case of air and  $\text{CO}_2$  ions it was found that the negative ions have the same mobility in air and that in each case there is an initial positive ion

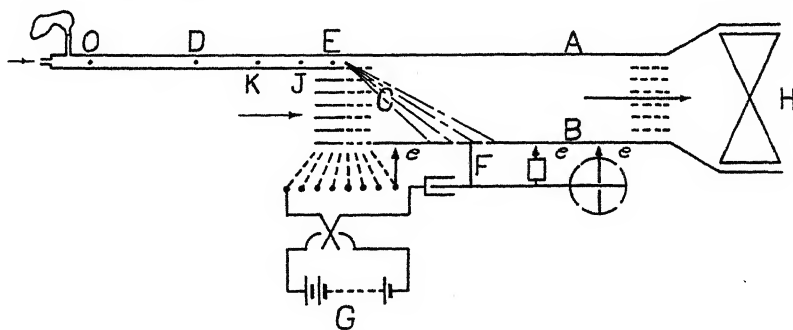


Fig. 1. Diagram of apparatus.

and a final positive ion, the former transforming into the second. In the case of actinium active deposit, two positive ions were found, one having a mobility of the order of that of the final positive air and  $\text{CO}_2$  ions and the other a mobility of a higher order.

In this article will be given the results of similar measurements in the case of argon and hydrogen ions.

<sup>1</sup> Erikson, Phys. Rev. 20, 117 (1922); 24, 502 and 622 (1924);  
Wahlin, Phys. Rev. 20, 267 (1922).

The method used is essentially the same as in the earlier work. The argon or hydrogen was passed from the containers through the tube *OE* (Fig. 1) where the ions were produced by means of the  $\alpha$ -rays from polonium. The rubber balloon at *O* served to indicate when the rate of flow was normal. The ions were carried with the stream and at *E* were drawn out of the argon and hydrogen gas by the electric field between *A* and *B* and passed through the air to the plate *B* where the current at

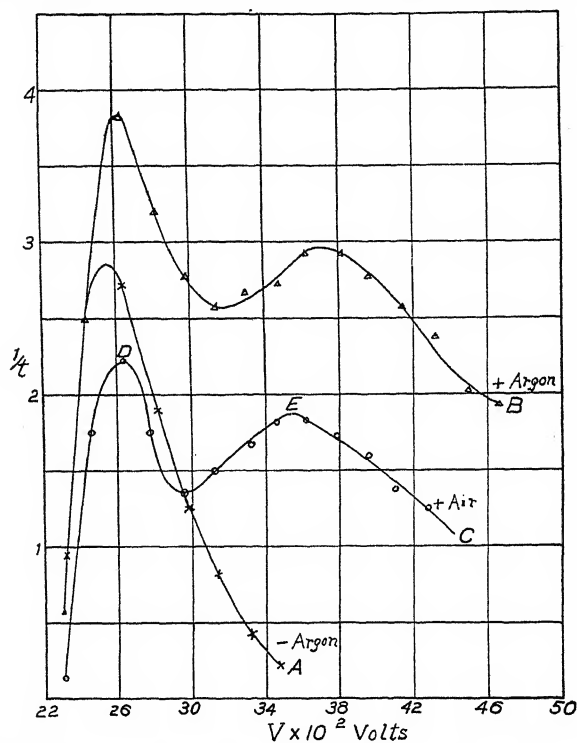


Fig. 2. Results for argon ions. Curve A for negative ion; Curve B for positive ion. Curve C is comparison curve for positive air ions.

*F* was measured for different potentials between the plates *A* and *B*. The velocity of the gases produced by the fan *H*, was of the order of 1500 cm/sec.

#### RESULTS IN THE CASE OF ARGON

The argon was supplied by the National Lamp Works of the General Electric Company, Cleveland, Ohio. The purity is given by the following analysis: argon 99 percent, nitrogen 0.9 percent, oxygen 0.1 percent. Curve A, Fig. 2, is for the negative argon ion and curve B is for the positive argon ion. Curve C is for the positive air ions and was obtained under similar conditions and is inserted for purposes of comparison. Maximum *D* is

for the initial air ion and maximum  $E$  is for the final air ion. As the ion mobility determines the position of the maximum, it is seen that the negative argon ion has the same mobility in air as the initial positive air ion and, therefore, the same as the negative air ion. It is also seen that there is a positive argon ion which corresponds to the initial positive air ion; also, that there is a positive argon ion which corresponds to the final positive air ion. On account of the limited supply of argon, it was not possible to repeat the measurement using younger or older argon ions and thus show that the first transforms into the second. That the first transforms in time to the second is, however, quite certain.

Since argon is a monatomic gas, these results show that an ion one atom large moves through air with the same mobility as the negative and initial positive air ions which are each one diatomic molecule large and also with the same mobility as the negative and initial positive  $\text{CO}_2$  ions which are each one triatomic molecule large. This is, therefore, additional evidence that all one molecule ions having equal charges have equal mobilities in air. The final argon ion is formed when the initial positive argon ion attaches itself to a neutral argon or air molecule.

#### RESULTS IN THE CASE OF HYDROGEN

The hydrogen used was electrolytic hydrogen for which the Commercial Gas Company reported a purity of 99.9 with a trace of  $\text{CO}_2$ , water vapor and oxygen. The gas passed from a commercial supply cylinder through the tube  $OE$ , Fig. 1, where it was ionized by means of the  $\alpha$ -rays from polonium, and the current-voltage curve at  $F$ , Fig. 1, was obtained just as in the case of argon. The results obtained in the case of hydrogen are shown graphically in Fig. 3. Curves  $A$  and  $B$  were obtained with the polonium at  $E$ , Fig. 1.  $A$  is for the negative ions and  $B$  for the positive ions. For curves  $C$  and  $D$  the polonium was at  $J$ , for curves  $E$  and  $F$  at  $K$ , for curves  $G$ ,  $H$ , at  $D$ , and for curves  $I$ ,  $J$  at  $O$ .

The upper curves correspond to the same positions as the curves immediately below, but are for ions produced in air instead of hydrogen; otherwise, the conditions were identical. It is seen that also in the case of hydrogen there is an initial positive ion and that it transforms into a final ion. It is evident from the curves that the transition is more slow in the case of the hydrogen ion than in the case of the positive air ion. It is also seen that the mobility of the initial and final positive hydrogen ions in air are the same as the mobilities in air of the initial and final positive air ions and of the negative air ion.

It is further seen that only one negative ion is formed in hydrogen, the same as in air. A marked difference, however, comes into evidence here,

in that the mobility of the negative hydrogen ion is higher than that of the initial positive hydrogen ion and the initial positive and negative air ions. The writer is unable to account for this difference. The negative ion, according to the author's view, is a hydrogen molecule which has gained an electron just as the initial positive hydrogen ion is the hydrogen molecule which lost an electron in the ionizing process. That the negative ion should move more rapidly in air than the initial positive hydrogen

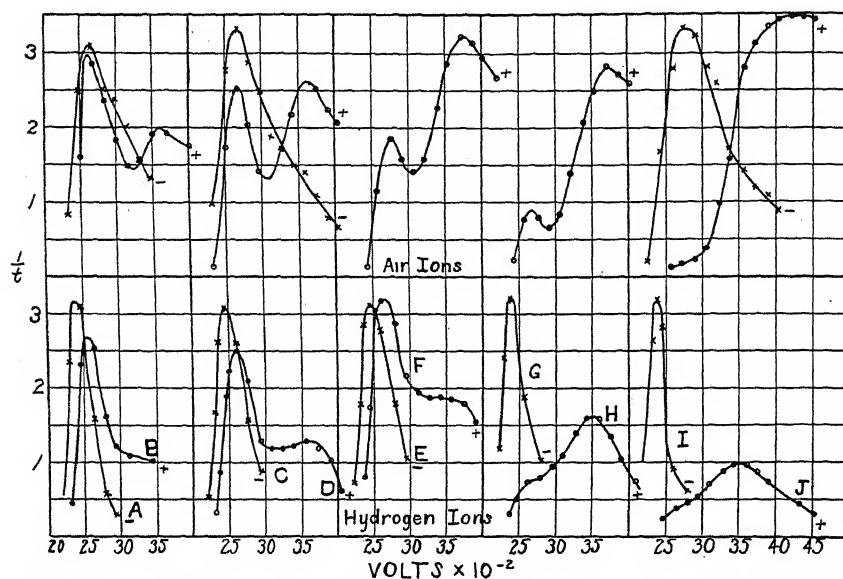


Fig. 3. Curves for hydrogen ions (below) and corresponding curves for air ions (above).

ions or the initial positive and negative air ions which are also each one molecule large is not, it would seem, to be expected, and is the first exception encountered by the writer to the view that all one molecule ions equally charged have the same mobility in air.

The author wishes to thank the Executive Committee of the Graduate School of the University of Minnesota for its financial aid in this research.

PHYSICAL LABORATORY,  
UNIVERSITY OF MINNESOTA.  
March 1, 1925

## EMISSION AND ABSORPTION BANDS OF CARBON DIOXIDE IN THE INFRARED

JOSEPH W. ELLIS

## ABSTRACT

The absorption spectrum produced by a 12 cm cell of  $\text{CO}_2$  gas, and the Bunsen flame emission spectrum, to  $3\mu$  were recorded by means of a new self-registering infrared quartz prism spectrograph of an auto-collimation type. A new weak absorption band was found at  $2.02\mu$  which forms a linear, though not a harmonic, frequency series with known bands at  $2.73\mu$  and  $4.25\mu$ . This was identified with a  $1.99\mu$  flame emission band, which had been assigned by Paschen to water vapor. The  $2.7\mu$  emission region was widely resolved into two components of practically equal intensities, with maxima at  $2.58\mu$  and  $2.76\mu$ , corresponding to maxima identified by Paschen with water vapor and  $\text{CO}_2$ , respectively. When the quartz prisms were replaced by a similar rock salt pair the  $4.4\mu$  emission occurred as a nearly symmetrical band, although Barker's measurements with high dispersion showed it to be double. Calculations of the Bunsen flame temperature from his observed separations gave  $2000^\circ\text{K}$ , in rough agreement with previous pyrometer determinations.

THREE regions of selective absorption due to carbon dioxide, with wave-length values for the maxima at approximately 14.7, 4.25 and  $2.7\mu$ , have been observed by numerous investigators.<sup>1</sup> Corresponding bands of emission have been found in the spectrum of the Bunsen flame by these and other investigators, and have been attributed universally to  $\text{CO}_2$ . Bjerrum<sup>2</sup> has predicted three characteristic vibrational frequencies in the near infrared for carbon dioxide on the basis of a triangular molecule. His attempt to identify the three bands mentioned above as these predicted frequencies met with some success in that the molecular heats at various temperatures calculated on the basis of these three vibrations check fairly well with observed values.

Whenever the dispersion was great enough, each of the carbon dioxide absorption bands appeared double, resembling in this respect the infrared absorption bands characteristic of diatomic gases. From its unusual behavior toward changes of temperature and pressure, Fr. Von Bahr<sup>1</sup> concluded that the double band at  $2.7\mu$  did not constitute a regular infrared doublet. Her conclusion has recently been verified by Barker,<sup>1</sup>

<sup>1</sup> Paschen, Ann. der Phys. und Chem. 50, 409 (1893); Trowbridge and Wood, Phil. Mag. 20, 898 (1910); Burmeister, Deutsch. Phys. Ges. 15, 589 (1913); Eva von Bahr, Deutsch. Phys. Ges. 15, 710 and 1150 (1913); Barker, Astrophys. J. 55, 391 (1922).

<sup>2</sup> Bjerrum, Deutsch. Phys. Ges. 16, 737 (1914).

who has shown with the use of especially ruled echelette gratings that both of the bands in this region are doublets with approximately equal frequency separations. Barker attempts to explain these two bands on a quantum theory basis, suggesting that each represents a fundamental of the same vibration, being caused by vibrational changes from state 0 to state 1, and from state 1 to state 2, respectively. He makes no attempt, however, to connect these with the bands at  $4.25$  and  $14.7\mu$ .

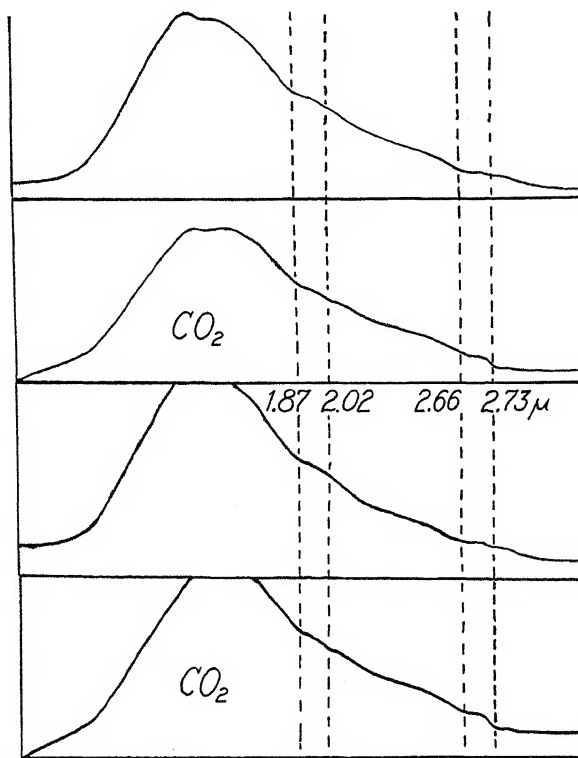


Fig. 1. Curves 1 and 3 show the distribution of energy from a tungsten lamp and the atmospheric absorption bands. Curves 2 and 4 show a deepening of the  $CO_2$  bands upon introduction of a 12 cm cell.

The writer has recently put a new self-registering infrared prism spectrograph (to be described elsewhere) to the task of searching for possible new absorption bands due to  $CO_2$ . That such a band was found at  $2.02\mu$  is due to the accuracy with which the instrument registers details.

The dispersing system of the recording spectrograph was of an auto-collimation type with a parabolic mirror of 3 cm aperture and 30.5 cm focal length and two prisms of quartz, with refracting angles of  $30^\circ$  and



60°, respectively. The prisms were fixed, but the spectrum to  $3\mu$  was caused to pass over the thermojunctions by a plane front surface mirror, the rotation of which was co-ordinated with the movement of the photographic plate upon which the energy distribution curves were traced.

Curves 1 and 3 of Fig. 1 show the distribution of energy from a tungsten lamp as produced by this spectrograph. In addition to the atmospheric water vapor absorption bands at 1.4, 1.87, and  $2.66\mu$ , and the  $\text{CO}_2$  band at  $2.73\mu$ <sup>3</sup> slight indication of another band at  $2.02\mu$  appears. When a 12 cm cell of cold  $\text{CO}_2$  gas was placed before the initial slit of the spectro-scope this latter band was unmistakably deepened as shown in curves 2 and 4. The carbon dioxide gas, generated in a Kipp generator by running dilute hydrochloric acid over calcium carbonate, was allowed to pass continually through the absorption cell during the production of a record. That the two  $\text{CaCl}_2$  drying tubes were effective in removing all water vapor, thus eliminating the possibility of attributing this  $2.02\mu$  band to that gas, is shown by the fact that the water vapor bands, cited above, were not deepened. Absorption at  $2.73\mu$  was, however, greatly increased.

The regular gradation of intensities for the 4.25, 2.73, and  $2.02\mu$  absorption bands suggests a three member series. The frequency differences between these bands are essentially the same (see Table I), but the usual harmonic relationships<sup>4</sup> existing among infrared vibrational bands are lacking. Because of its intensity and its wave-length values, the  $14.7\mu$  absorption maximum does not seem to belong to this group of bands.

TABLE I  
*Series of carbon dioxide absorption bands*

$\lambda$	$\nu \times 10^{-11}$	Diff.
$4.25\mu$	706	
2.73	1099	393
2.02	1485	386

In the emission spectrum of the Bunsen flame we should expect to find a maximum corresponding to this  $2.02\mu$  absorption band. Fig. 2

<sup>3</sup> Hettner's value *Zeits. f. Phys.* **1**, 351, (1920) for the  $2.66\mu$  water vapor band and Barker's value for the  $2.73\mu$   $\text{CO}_2$  band were used as calibration points in this region.

<sup>4</sup> Coblenz, Publication of the Carnegie Institution, **35**, (1905); Mandersloot, Dissertation, Amsterdam (1914); Brinsmade and Kemble, *Proc. Nat. Acad.* **3**, 420 (1917); Hettner, loc. cit.<sup>3</sup>; Kratzer, *Zeits. f. Phys.* **3**, 460 (1920); Schaefer and Thomas, *Zeits. f. Phys.* **12**, 330 (1924); Ellis, *J. Opt. Soc. Amer. and R.S.I.*, **8**, 1 (1924).

shows three independent records of the Bunsen flame emission. The band at  $1.99\mu$  is doubtless this maximum. Table II shows the co-ordination of the emission bands with their corresponding absorption bands.

TABLE II

*Emission bands in spectrum of Bunsen flame*

Emission	Absorption	Substance	Water absorption
$1.40\mu$	$1.40\mu$	water vapor	$1.48\mu$
1.79	1.87	"	1.98
2.58	2.66	"	2.98
1.99	2.02	CO <sub>2</sub>	
2.76	2.73	CO <sub>2</sub>	

Using fluorite prisms, Paschen<sup>5</sup> observed three regions of characteristic emission from the Bunsen flame, and gives the following values for their maxima:  $1.38$ ,  $1.83$ , and  $2.77\mu$ . Later, he studied these with various

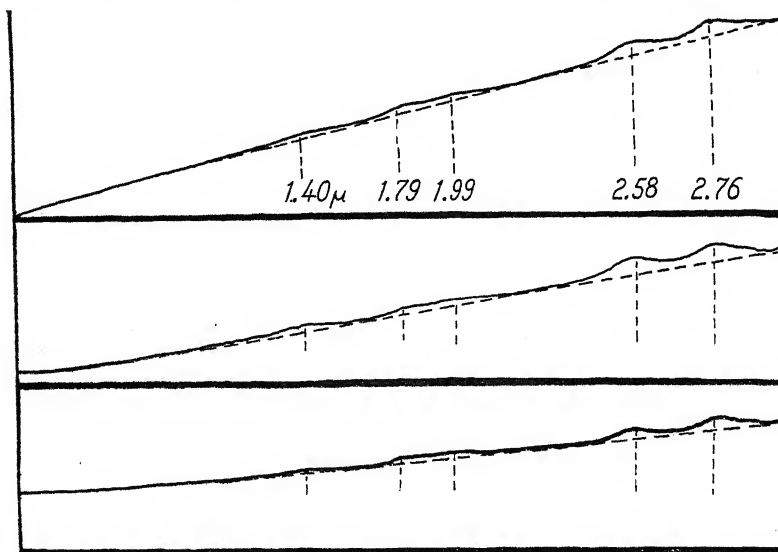


Fig. 2. Emission spectrum of the Bunsen flame obtained with quartz prisms. The slope of the records was produced by the galvanometer zero shift.

types of gratings and found them resolved into components as follows:  $1.35$  and  $1.42\mu$ ;  $1.803$ ,  $1.86$ , and  $1.966\mu$ ;  $2.51$ ,  $2.70$ , and  $2.84\mu$ . He found these to be characterized by "Knicken" and "Ecken," and suggested a possible line structure in the bands. He attributed all of the maxima, with the exception of the  $2.70\mu$  band, to water vapor, since they also occurred in the oxy-hydrogen flame. The  $2.70\mu$  band was identified with CO<sub>2</sub> gas, which also occurred with diminished intensity in the oxy-hydrogen flame.

<sup>5</sup> Paschen, *Ann. der Phys. und Chem.* **52**, 209 (1894).

The emission bands of the present investigation agree, in general, with those observed by Paschen, except that no maximum was observed corresponding to his  $2.84\mu$  value, and the  $1.99$  peak is identified with  $\text{CO}_2$  instead of with water vapor.

Fig. 3 shows the Bunsen flame emission spectrum as obtained when two rock salt prisms were used in place of the quartz pair. Since the dispersion of rock salt in the region of  $2.7\mu$  is only one tenth of that of quartz, the  $2.58\mu$  water vapor band and the  $2.76\mu$  carbon dioxide band appear as a single unresolved maximum. It may be pointed out that when reference is made to the  $2.7\mu$  emission band of the Bunsen flame

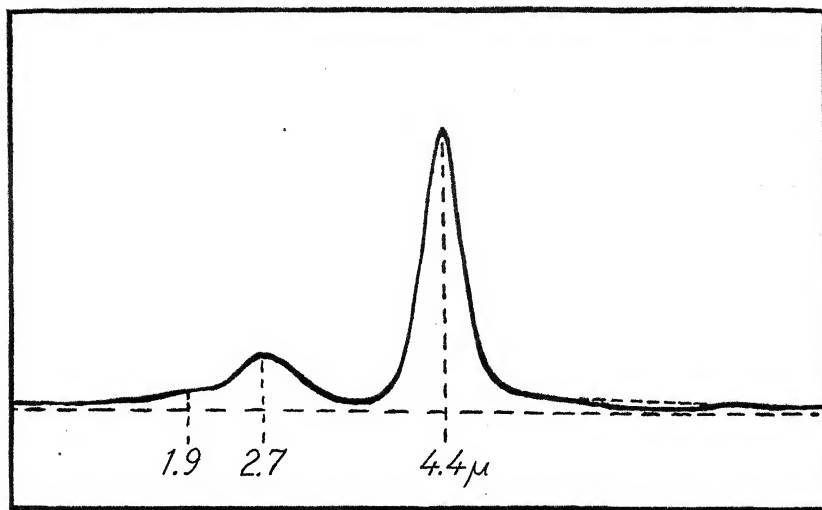


Fig. 3. Emission spectrum of the Bunsen flame obtained with rock salt prisms.

it is almost always attributed to carbon dioxide alone, whereas Fig. 2 shows that water vapor and carbon dioxide contribute almost equally to this emission. Fig. 3 shows the bands of shorter wave-lengths unresolved with a maximum at about  $1.9\mu$ .

The  $4.4\mu$  region of emission occurs as a band of considerable symmetry although it is possible that absorption due to a protective varnish on the prism faces may have modified the curve to some extent. This varnish was the solution of pyroxylin in amyl acetate used by Adam Hilger, Ltd. Although the energy distribution curve is only slightly modified when the light passes through two layers of this varnish, deep absorption bands at  $3.4\mu$  and  $6.7\mu$ , characteristic of practically all organic materials,<sup>6</sup> do occur when the light traverses eight layers, as it does in this case.

<sup>6</sup> Coblentz, loc. cit.<sup>4</sup>

The latter band appears in Fig. 3 as a broad minimum of transmission in the continuous black body radiation<sup>7</sup> of the flame.

Barker<sup>1</sup> has shown by taking account of the reversal due to absorption, that the  $4.4\mu$  emission band is double with maxima at  $4.225$  and  $4.38\mu$ . He also found the corresponding absorption band double with maxima at  $4.22\mu$  and  $4.28\mu$ . These two doublet separations are consistent with the formula<sup>8</sup>

$$\sqrt{T} \cdot \lambda_1 \lambda_2 / (\lambda_1 - \lambda_2) = \text{a constant}$$

which connects such separations  $(\lambda_1 - \lambda_2)$  with the absolute temperature  $T$ , on the assumption that the temperature of the Bunsen flame is about  $2000^\circ\text{K}$ . Féry<sup>9</sup> has determined this temperature with an optical pyrometer and found it to be  $2144^\circ\text{K}$ , while Schmidt's<sup>10</sup> determination was somewhat lower,  $1913^\circ\text{K}$ .

If the primary separation of the double doublet found by Barker<sup>1</sup> at  $2.7\mu$  were a regular infrared doublet of the Bjerrum type, the corresponding emission doublet, calculated from the above equation, would have a wave-length separation equal to the total spacing between the  $2.58\mu$  water vapor and the  $2.76\mu$  carbon dioxide bands.

DEPARTMENT OF PHYSICS,  
UNIVERSITY OF CALIFORNIA, SOUTHERN BRANCH  
June 20, 1925

<sup>7</sup> Paschen, *Ann. der Phys. und Chem.* 50, 1 (1894).

<sup>8</sup> Eva von Bahr, *Phil. Mag.* 28, 71 (1914).

<sup>9</sup> Féry, *Jour. de Phys.* 4, 6 (1907).

<sup>10</sup> Schmidt, *Ann. der Phys.* 29, (1909).

THE EFFECT OF LIGHT ON THE THERMAL  
CONDUCTIVITY OF SELENIUM

BY R. E. MARTIN

## ABSTRACT

Both thermal and electrical conductivities were measured for the same thin strip of Se, in order to compare the effect of illumination on both. The cells were made by winding a double spiral of Pt or Ni wire on a mica form, then pressing melted Se into a thin layer over and between them by means of another sheet of mica. The thermal effect was measured by heating one winding *CD* by an electric current and using the other *AB* as a resistance thermometer. The Se was rendered light sensitive by suitable heat treatment and the cell was placed in a well insulated box kept at 0° C. Correcting for the heating effect of the light, the rate of rise of temperature of *AB* was 15 to 30 percent greater with the illumination than without, the percentage change for each cell being about half that observed for the electrical conductivity of the same cell for the same illumination. A cell which was not sensitive electrically was also not sensitive thermally. By using various color screens it was found that as in the case of the electrical sensitivity, the red end of the spectrum is more effective than the shorter wave-lengths. Sieg failed to find this effect and explained his negative result as due to the absence of an electric field, but an electric field applied by means of the winding *AB* was found to have no effect on the thermal conductivity. These results furnish additional evidence that thermal and electrical conductivities in metals both depend, at least to a considerable extent, upon the same factors.

## INTRODUCTION

TWO theories based on the electron theory of matter, have been proposed to account for the sensitiveness of the electrical resistance of metallic selenium to illumination, Marc<sup>1</sup> and others have obtained evidence that there exists two (possibly more) forms of metallic selenium of widely different electrical resistivity. It was assumed that illumination brings about a transformation from the less to the more conducting of the two. This theory has been amplified and put into mathematical form by Brown<sup>2</sup> who assumes the existence of three forms, selenium A, B, and C. The second theory, which is quite in harmony with the first, was introduced by Pfund.<sup>3</sup> This theory assumes that the effect is due to a resonance of the electrons in the atom, occasioning explosions which lead to an increase in the number of conducting electrons. This view has found favor with several experimenters, particularly with Ries<sup>4</sup> by whom a great

<sup>1</sup> Marc, Monograph on the Physical-Chemical Properties of Selenium (1907) Leopold Voss, Hamburg.

<sup>2</sup> Brown, Phys. Rev. 32, 237 and 252 (1911).

<sup>3</sup> Pfund, Phys. Rev. 28, 324 (1909).

<sup>4</sup> Ries, Monograph on the Electrical Properties of Selenium (1908), Nicholas, Berlin.

amount of valuable work has been done. The theory deserves attention for various reasons. First, the ultimate explanation found must be in terms of the electron theory if that theory is to remain a permanent part of our physical science. Second, the idea of resonance appears plausible.

Now on the basis of the electron theory Lorentz,<sup>5</sup> Bohr,<sup>6</sup> Richardson,<sup>7</sup> and others have attempted to explain the fact that good conductors of electricity are also good conductors of heat. The law of Wiedemann and Franz,<sup>8</sup> which was discovered experimentally, states that the ratio of the thermal to the electrical conductivity has the same value at the same temperature for all good conductors. Lorenz<sup>9</sup> later discovered that for different temperatures the ratio of the thermal and electrical conductivity is proportional to the absolute temperature. For poor conductors this relation is not constant, but even for such substances, if the conductivity is even partially electronic, then any agency that changes the number of free electrons in the substance should change both the thermal and the electric conduction.

While the change in the electrical conductivity of selenium under the influence of light has been established beyond question, the effect of light on the thermal conductivity has not been disposed of so satisfactorily. Bellati and Lussana<sup>10</sup> obtained results which they interpreted to show that the thermal conductivity varied under the influence of light at about the same rate as the electrical conductivity. Sieg<sup>11</sup> found that there was no measurable change in the thermal conductivity of selenium when illuminated. Later, Nannei<sup>12</sup> used the method of Bellati and Lussana, that of Sieg and also one of her own. She found that the effect was less than that on the electrical conductivity but was always present and that it increased with a decrease of temperature. Now it seemed to the writer that in all of these experiments the amount of selenium which was exposed to the light was a very small part of the selenium actually conducting heat. Particularly is this so if the effect is a surface phenomenon. With this idea in mind a plan was sought which would subject the same amount of illuminated selenium to heat conduction as to electrical conduction.

<sup>5</sup> Lorentz, *Theory of Electrons*, 67 and 266 (1909), Teubner, Leipzig.

<sup>6</sup> Bohr, *Studier over Metallernes Elektrontheori*, Copenhagen (1911).

<sup>7</sup> Richardson, *Phil. Mag.* **23**, 594 (1912).

<sup>8</sup> Wiedemann and Franz, *Ann. de Chimie* **12**, 107 (1854).

<sup>9</sup> Lorenz, *Ann. der Phys.* **147**, 429 (1872).

<sup>10</sup> Bellati and Lussana, *Gazz. Chim. Ital.* **17**, 39 (1887); *Atti. R. Ist. Ven.* **6**, 19 (1887); and *Beibl. zu d. Ann.* **11**, 818 (1887).

<sup>11</sup> Sieg, *Phys. Rev.* **6**, 213 (1915).

<sup>12</sup> Nannei, *N. Cimento* **20**, 185 (Nov.-Dec. 1920).

## CONSTRUCTION OF CELLS

The cells used were constructed in various ways which suggested themselves as the work progressed, but the winding of the wires which formed the electrodes was practically the same for all.

In Fig. 1,  $AB$  is a continuous wire wound around the insulator  $WW$  with a spacing giving about four turns to the centimeter.  $CD$  is another continuous wire wound around the same insulator, the turns being equally spaced between those of  $AB$  and thus insulated from  $AB$ . A layer of crystalline selenium was then formed over the wires and insulator. The wires used on three of the cells were of platinum, while on all of the rest they were of nickel. The latter was used because nickel has the higher temperature coefficient of resistance, it appears to oxidize less

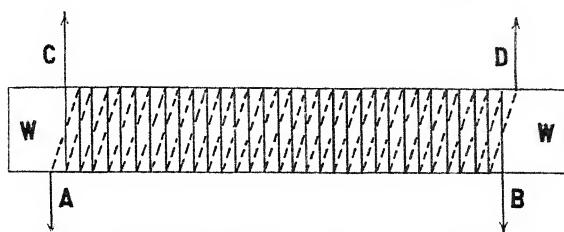


Fig. 1. Diagram showing windings of sensitive cells.

readily than platinum, and it is less expensive. Dieterich<sup>13</sup> found that it was just as satisfactory for winding cells as was platinum. The insulators used were usually of mica, but soapstone and glass was also used for some.

A strip of mica 10 cm long, 1.5 cm wide and .05 cm thick was placed between the two halves of a hardwood cylinder which had previously been turned down to the proper size and then cut lengthwise into halves. About eight threads to the centimeter were cut on the cylinder and mica and the halves of the cylinder were then separated from the mica and the windings put on the mica form. Finely pulverized amorphous selenium was then poured onto the prepared mica form which was then placed on a metal plate over a Bunsen flame. After the selenium had melted, a second strip of mica was placed on top of the selenium and the two strips of mica were pressed firmly together. This forced the selenium to spread out into a very thin layer. This pressure was maintained while the cell was cooled rapidly. The cell was then put into an electric furnace whose temperature was 210°C and kept there for thirty minutes, after which the temperature of the furnace was slowly lowered to 180°C. The cell was kept at 180°C for ten hours and then placed immediately in a

<sup>13</sup> Dieterich, Phys. Rev. 4, 467 (1914).



glass container which had been previously dried and which was air tight. This container was placed in a light tight box and kept there for forty-eight hours before testing. All of the cells made in this manner were found to be light sensitive electrically.

#### METHOD OF MEASURING VARIATION IN THERMAL CONDUCTIVITY

The arrangement of the apparatus for measuring the variation in both the electrical and thermal conductivity is shown in Fig. 2. The D'Arsonval galvanometer  $G$ , whose figure of merit was of the order of  $10^{-8}$ , was mounted on a solid stone column which rested on the concrete floor

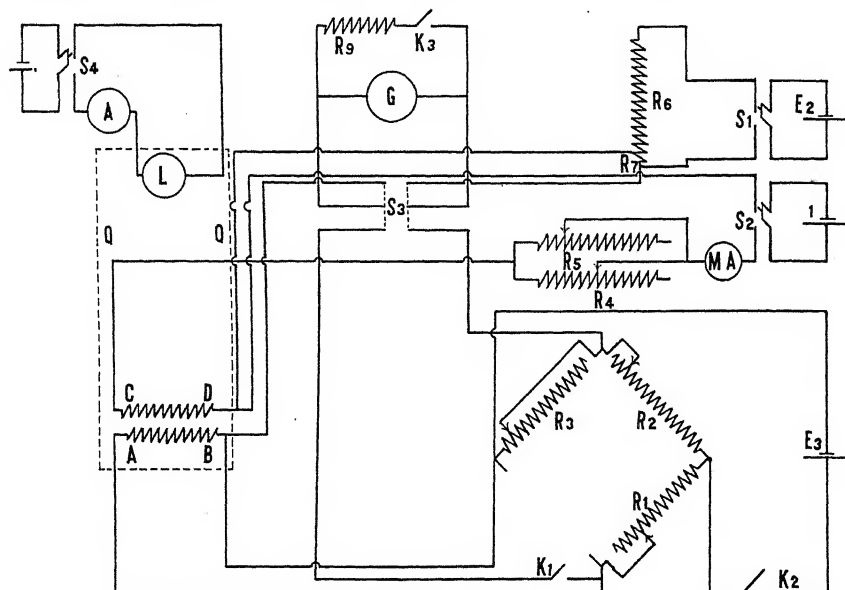


Fig. 2. Diagram of electrical connections.

of the basement room in which the experiment was conducted. The galvanometer shunt  $R_9$  was used during preliminary work only, and no observations were taken when the galvanometer was shunted.  $R_1$ ,  $R_2$ , and  $R_3$  form three of the arms of a Wheatstone bridge of which the winding  $AB$  forms the fourth arm.  $K_1$  and  $K_2$  are contact switches whose normal position is open.  $MA$  is a milli-ammeter graduated to read directly to 5 milli-amperes.  $R_4$ ,  $R_5$ ,  $R_6$ ,  $R_7$ , and  $R_8$  are variable resistances.  $S_1$ ,  $S_2$  and  $S_4$  are double-pole single-throw switches, while  $S_3$  is a double-pole double-throw switch. The battery thrown in by switch  $S_1$  is a 6-volt storage battery;  $E_2$  is a 2-volt storage battery;  $E_3$  is a dry cell, and the voltage applied by closing  $S_4$  is that of a 110 d.c. circuit.  $A$  is an ammeter and  $L$  an incandescent lamp.  $BB$  is a light tight box. The cell was

placed in a specially designed calorimeter and kept at ice temperature. The details of the arrangement of the cell, calorimeter, and light tight box are shown in Fig. 3.

The walls  $WW'$  of the chamber fitted snugly on top of the calorimeter below, which was a double walled vessel made of copper, with ice  $II$  packed between the walls and with hair-felt  $HH$  about 5 cm thick surrounding it. The calorimeter, together with its wrappings, was placed in a suitable wooden box. By this arrangement a constant temperature was maintained for as much as twelve hours without disturbing the parts to repack with ice. The light was placed at  $L$  and the selenium cell to be tested at  $SS$ . Light tight boxes 6 cm by 10 cm and of various lengths, varying from 30 to 100 cm were used.

The plan followed was to measure the resistance of  $AB$  after the cell had stood for several hours at the temperature of melting ice. Then a known current was sent through  $CD$  and the rate of rise in temperature of  $AB$  determined by observing the rate of increase of its resistance. This was then repeated with the cell exposed to the light. If illumination increases the thermal conductivity of the selenium then the resistance should increase faster when the cell was exposed to the light. A correction was made for the heat delivered to  $AB$  by the light rays from  $L$ .

The ratio in the bridge was kept at 1000 to 1 and the smallest adjustment in the bridge arm was 1 ohm, so a change of resistance of .001 ohm could be measured directly. The bridge was balanced carefully by adjusting the bridge arm until the addition of 1 ohm would cause a reversal in the deflection of the galvanometer. An additional ohm was then added to the bridge arm, and a stop clock was started at the same instant that  $S_2$  was closed. The keys  $K_2$  and  $K_1$  were then tapped momentarily at short intervals and the instant noted when the bridge was again balanced. Another ohm of resistance was then added to the bridge arm and again the keys were tapped at short intervals and the time when the bridge was again balanced noted. This process was continued as long as the resistance of the wire  $AB$  showed an appreciable increase. Similar observations

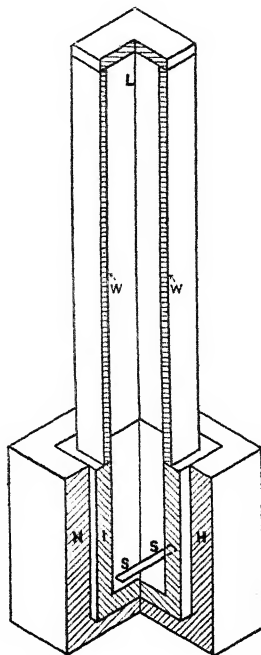


Fig. 3. Insulated box in which cell  $SS$  was placed.

were made using the same heating current, but with the cell illuminated by  $L$ .

After the cell had again come to thermal equilibrium with its surroundings, with no heating current through  $CD$ , the light from  $L$  was allowed to fall on  $AB$  and the rate at which its resistance increased was determined. From these data the rate of increase of the resistance due to the change in conductivity of the selenium was determined.

The method here employed for determining the change in resistance of  $AB$ , while not as accurate, as far as the numerical value of the resistance itself is concerned, as the fall of potential method or some of the other methods of measuring a low resistance, will detect, it is believed, a change in resistance more precisely in point of time than would any of the other methods. The initial resistance of the electrode  $AB$  must be the same in each case and its surroundings must be in thermal equilibrium with it. For this reason the cell was kept in an ice chamber during the course of a set of observations and sufficient time was allowed between readings for thermal equilibrium to be established. Also,  $K_2$  must not be depressed for any considerable length of time or the heat generated in  $AB$  by the current from  $K_3$  will be sufficient to obscure the effects produced by the heat conducted through the selenium from  $CD$  to  $AB$ . The function of  $R_3$  (not shown in Fig. 3) is to keep this current very small at all times, but even then care must be exercised or its effects will be disturbing.

#### ELECTRICAL CHARACTERISTICS OF THE CELLS USED

All of the cells, except D, used in this set of experiments were high resistance, positive, light-sensitive cells. This method can only be employed with cells of high resistance between electrodes  $AB$  and  $CD$ , for if the resistance by this path is not extremely large compared with the resistance of the wires themselves then the heating current which is supposed to heat  $CD$  will be partially shunted through  $AB$  and cause the resistance of  $AB$  to increase. This fact was verified several times during the course of the work when an attempt was made to experiment with a light negative cell whose resistance was very low. The electrical characteristics of the cells used are shown in Table 1.

TABLE I  
*Electrical characteristics of the cells used*

Cell	Dark resistance	Light resistance	Sensitivity
A	13,870 ohms	6,950 ohms	49.9 percent
B	11,280	4,870	56.9
C	2,230	1,520	31.8
D	1,787,000	1,787,000	00.0
E	3,140	2,280	27.4
F	13,210	7,140	45.8
G	8,260	3,190	61.4

## EXPERIMENTAL RESULTS

In the case of cell C, with a 25 watt lamp at  $L$  and a heating current of 600 milli-amperes through  $CD$ , the results shown in Fig. 4 were obtained.

Curve 1 shows the rate the resistance increased when the cell was exposed to the light, while curve 2 shows the same when the cell was in the dark. Curve 3 shows the effect of the heat energy in the light rays

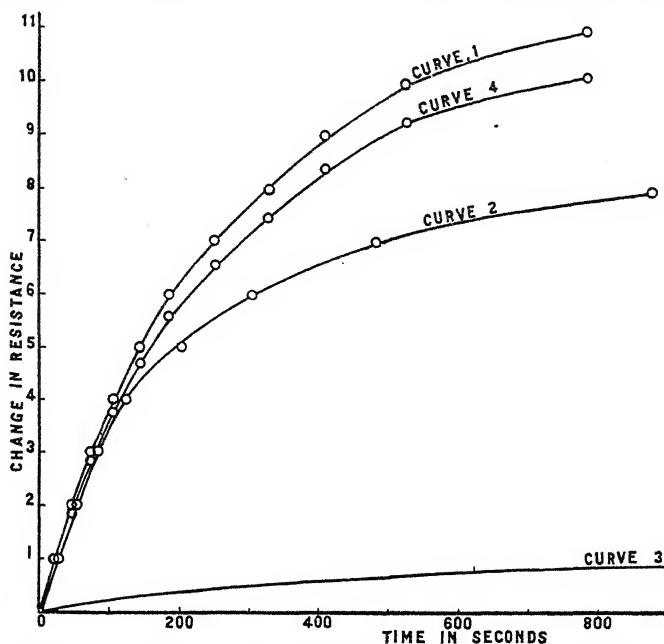


Fig. 4. Results for cell C. Curves 2 and 4 show change of resistance with time due to thermal conduction alone, curve 4 for illuminated cell, curve 2 for dark cell.

from  $L$  upon the resistance  $AB$ . By subtracting the ordinates of curve 3 from the corresponding ordinates of curve 1 the ordinates of curve 4 were obtained. Curve 4 when compared with curve 2 shows the effect of the light on the thermal conductivity of the selenium.

Fig. 5 shows the corrected curves for the data obtained when cell A was tested. Similar results were obtained for the other light positive cells tested.

It appears from the above examples that light does affect the thermal conductivity of selenium. This effect, while possibly not as great as it is in the case of the electrical conductivity, is of appreciable magnitude. The following two factors should cause the thermal effect to be less than the electrical. First, since the electrical conduction is entirely electronic

any change in the number of free electrons would affect the electrical conduction directly, while thermal conduction in selenium is probably partly molecular and partly electronic; hence, when the number of free electrons is changed only one of these factors is affected. The freeing of a given number of electrons would then affect the electrical conductivity to a greater extent than it would the thermal conductivity. Second, the transfer of electricity is a much more rapid process than the transfer of

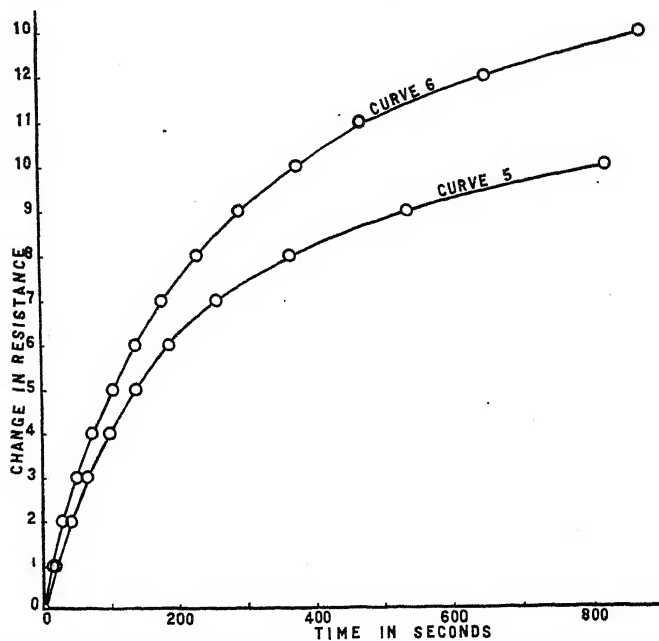


Fig. 5. Change of resistance of cell A with time, due to thermal conduction alone, in the dark (curve 5) and when illuminated (curve 6).

heat and since the effect of light on selenium is a surface effect to a large extent, a gradual lowering of the electrical and thermal resistance of the surface of the cell would result in more rapid change in the flow of electricity than in the flow of heat.

#### THE EFFECT OF AN ELECTRIC FIELD

It has been suggested by Sieg<sup>11</sup> that perhaps the reason why illumination affected the electrical conductivity of selenium and did not, as far as his experiments showed, affect the thermal conductivity, could be explained in the following manner. When the variations in the electrical conductivity were being measured the selenium was necessarily in an electric field and the electrons being rendered unstable in the atom by the action of light were then drawn from the atom by the action of the

electric field. On the other hand, when the effect of illumination on the thermal conductivity was studied the selenium was not in an electric field and, consequently, even though the electrons became unstable in the atoms, due to the action of the light, they would not necessarily leave the atom and thus become effective in the conduction of heat. Now by the present method the selenium was always in the electric field produced by the combined action of  $E_1$  and  $E_3$ .

To test this hypothesis further it was decided to determine the variation in the thermal conductivity when the cell was illuminated and in an additional electric field. The electric field applied was the field used when the variation in the electrical conductivity was determined, it being merely necessary to have switch  $S_1$  in Fig. 2 closed while the observations on the thermal conductivity were taken. Typical sets of observations are shown in Table II.

TABLE II

	Change in res. of $AB$	Time elapsed after starting heating current		
		Field zero	Field direct	Field reversed
In the dark	.001 ohm	36 sec.	39 sec.	38 sec.
	.002	80	74	76
	.003	135	131	134
Illuminated	.001	21	21	20
	.002	49	48	45
	.003	78	77	70

These observations indicate that a variation in the electric field produced no appreciable effect on the thermal conductivity of the selenium either when the cell was in the dark or when it was illuminated. A small heating current of only 100 milli-amperes was used so that ample time would be available for detecting any possible change in the thermal conductivity. Since it is evident that the light itself did have an appreciable effect on the thermal conductivity, the phenomenon described in this paper seems to be due to the action of the light alone and not to the action of the electric field.

#### THE EFFECT OF VARIOUS COLORED LIGHTS

It was thought that perhaps the effect on the thermal conductivity might vary with the color of the light with which the selenium was illuminated. To test this hypothesis light was transmitted through various glass filters which were obtained from the Corning Glass Works, and the effects observed. The current through the lamp was first adjusted so that the transmitted beam in each case was of a given heating intensity, by allowing the light to fall on a thermopile which was in series with the

galvanometer described above. The wave-length transmission curves for the different glasses used are given in Bulletin No. 148, Bureau of Standards Publication, issued March 19, 1920. No attempt was made to study the variation with color exhaustively but only to determine the general trend. The observations on two cells are given in Tables III and IV.

TABLE III  
*Effect of various colored lights of equal heating intensity on cell A*

Change in res. of AB (ohm)	Time elapsed in seconds after heating current started							
	Dark	Blue G585	Red G24	Red G24B	Orange G34	Yellow G34B	Purple G55A	Red- purple G586A
.001	19	17	15	12	12	13	13	12
.002	35	31	...	23	25	28	27	27
.003	54	50	45	38	41	44	42	46
.004	75	71	63	50	58	63	58	65
.005	100	106	91	76	84	95	82	96
.006	142	139	116	98	108	125	106	130
.007	176	174	144	126	134	152	139	158
.008	222	221	176	156	169	200	163	201
.009	287	284	215	203	210	264	201	268
.010	450	445	278	255	276	342	255	389

TABLE IV  
*Effect of various colored lights of equal heating intensity on cell C*

Change in res. of AB (ohm)	Time elapsed in seconds after heating current started							
	Dark	Blue G585	Red G24	Red G24B	Orange G34	Yellow G34B	Purple G55A	Red- Purple G586A
.001	18	13	10	12	...	...	11	15
.002	31	24	...	20	...	...	20	26
.003	45	38	30	...	...	...	30	35
.004	59	51	42	40	52	45	40	45
.005	76	65	54	52	68	58	51	...
.006	96	80	68	65	83	69	65	69
.007	125	102	86	80	100	89	78	...
.008	163	124	103	92	122	102	93	100
.009	203	...	123	108	143	117	108	113
.010	263	170	144	129	165	135	126	132
.011	...	210	168	150	192	152	143	148
.012	...	248	195	172	225	175	167	173
.013	...	288	232	199	260	198	190	201
.014	...	...	272	227	292	225	214	229
.015	...	...	328	262	345	264	246	267
.016	...	...	...	...	...	314	281	315

These observations indicate that the effect of light on the thermal conductivity of selenium is dependent both upon the color of the light and upon the characteristics of the selenium cell used. All cells seem to be affected more by red light than by blue light, but some cells are affected more than others by light which lies toward the middle of the visible spectrum. Almost all cells for which published data are available show a



maximum electrical sensitivity in the red end of the spectrum and some also show another maximum toward the blue end; however, this second maximum is usually much less than the former. The present observations show that the thermal sensitivity is also a maximum in the red end of the spectrum.

#### EFFECT ON A CELL THAT IS NOT LIGHT-SENSITIVE ELECTRICALLY

In order to test qualitatively the relation between the thermal sensitivity and the electrical sensitivity of selenium, a cell D was built in a manner similar to that used for all of the others excepting that the annealing process was omitted and hence the cell on testing proved to be non-sensitive electrically to light radiations. The cell was tested in the same manner as all of the other cells. Observations were taken for various heating currents through *CD*. No change in thermal conductivity was observed. Hence, annealing the selenium renders it not only light sensitive electrically but also light sensitive thermally. This is additional evidence that the two phenomena depend, at least to some extent, upon the same factors.

#### DISCUSSION

Either theory, the one suggested by Brown<sup>2</sup> or the one suggested by Pfund,<sup>3</sup> may account for the change in thermal conductivity of the selenium when illuminated. It seems, however, that the theory suggested by Brown is the more plausible. If, as Pfund suggests, the atoms of the selenium become unstable under the action of light and then some of them explode, thus liberating electrons, it seems that there should be more explosions under the action of an electric field than in the absence of such a field. This conclusion was not borne out in the present work. Brown, in his hypothesis, does not suggest anything that would lead one to suppose that the presence of an electric field would affect the rate of change of the different forms of selenium.

In conclusion, I wish to thank Dr. A. L. Foley, who suggested this problem, and other members of the faculty of the Department of Physics for valuable suggestions and encouragement during the various phases of the experiment.

PHYSICAL LABORATORY,  
INDIANA UNIVERSITY,  
July 20, 1925.

THERMO-ELECTRIC EFFECT IN SINGLE  
CRYSTAL ZINC WIRES

BY ERNEST G. LINDER

## ABSTRACT

The crystals were prepared by the Czochralski method, drawing each in the form of a wire through a 2 mm hole in a mica disk which floated on the surface of the zinc, kept just a few degrees above its melting point. After slight amalgamation, the crystals split readily along the basal plane, normal to the vertical axis. The angle between this axis and the axis of the wire is the orientation  $\theta$  of the crystal. Each end of a crystal was sealed with cadmium into a copper block, one of which was kept at  $0^\circ\text{C}$ , the other at a temperature  $T$ , varied up to  $290^\circ\text{C}$ . The ratio of thermo-e.m.f.  $E$  to  $T$  is found not to be a linear function of  $T$  but to increase with  $T$  more rapidly. The curves for the higher values of  $\theta$  lie above those for lower values, so that with a circuit of differently oriented crystals the e.m.f. is directed, at the hot junction, from the crystal of higher to that of lower orientation. For wires with  $\theta=14^\circ$  and  $\theta=86.5^\circ$ , the e.m.f. with  $T=250^\circ$  would be  $6.50 \times 10^{-4}$  volt. The neutral temperature ( $dE/dT=0$ ) decreases from about  $500^\circ$  for  $\theta=14^\circ$  to  $40^\circ$  for  $\theta=86.5^\circ$ .

THE production of single crystal metal specimens and the determination of various physical constants in different directions in such crystals have recently claimed the attention of numerous investigators.<sup>1</sup> Very little work has been done, however, on the thermo-electric effects in metal crystals. It was the purpose of this investigation to study the thermal e.m.f. in single crystal zinc wires as dependent on the orientation of the space lattice relative to the axis of the wire.

The crystals were made by a method devised by Czochralski<sup>2</sup> whereby metallic crystals in the form of wires are drawn from a melt through a hole in a mica disk floating upon its surface. The zinc was kept just a few degrees above the melting point. The mica disk was large enough to cover the entire surface and thus prevent oxidation. The hole in the disk was about 2 mm in diameter and served to make the crystal surface more uniform. The velocity of drawing out the crystal varied between 6 and 10 mm/sec. depending upon the temperature of the melt and other

<sup>1</sup> Zeits. f. Instrumentenkunde 3, 152 (1925);  
Gruneisen and Goens, Zeits. f. Phys. 29, 141 (1924); 26, 235 (1924);  
Bridgman, Proc. Nat. Acad. Sci. 10, 411 (1924);  
M. Polanyi, Zeits. f. Elektrochem. 28, 16 (1922);  
E. v. Gomerz, Zeits. f. Phys. 8, 184 (1922);  
M. Polanyi and Schmidt, Zeits. f. Phys. 12, 58 (1922).  
<sup>2</sup> Czochralski, Zeits. f. Phys. Chem. 92, 219 (1918).

factors. It was found that by starting crystals on a copper wire and drawing them out at an excessive rate, crystals of a varying orientation could be formed. (The orientation of a crystal is defined as the angle between the vertical (hexagonal) axis of the zinc and the direction of the length of the wire.) At the beginning of this rapid growth the orientation was approximately  $90^\circ$  and as the growth progressed it decreased, reaching about  $45^\circ$  when the wire was 25 cm long. By cutting off this crystal at the point having the desired orientation and starting a new crystal upon it, a crystal wire having any orientation between  $45^\circ$  and  $90^\circ$  could be obtained. To obtain orientations below  $45^\circ$ , a crystal having approximately  $45^\circ$  orientation was bent near the end so that its basal plane was inclined at the desired angle with the surface of the melt. Merck "very pure" zinc was used and no trouble due to impurities was encountered.

It was discovered that by slightly amalgamating the crystals with mercury they became brittle and could easily be split along the basal plane with a sharp knife. The normal to this basal plane is the vertical axis, and the orientation could then be easily determined by measuring the angle of inclination of this axis with respect to the axis of the wire by means of a reflected light beam.

The thermo-electric e.m.f., which was measured against copper, was determined by connecting the couple in series with a high resistance galvanometer calibrated for voltage. The crystal *Z*, Fig. 1, was enclosed in a glass tube for protection, and the two ends sealed with cadmium into cylindrical cavities in copper blocks. One of these blocks, *L*, contained the cold junction and was immersed in melting ice; the other, *U*, contained the hot junction and was heated by means of a heating coil wrapped around it; its temperature was measured by a mercury-in-glass thermometer *T*, inserted in a cavity in the block.

Fig. 2 shows the series of curves obtained for crystals of different orientations. The e.m.f. is considered positive when it acts from the hot to the cold junction through the zinc. It will be noticed that, within the observed temperature range, for a circuit composed of two crystals of different orientations the current would flow across the hot junction from the crystal having the lower orientation to that having the higher.

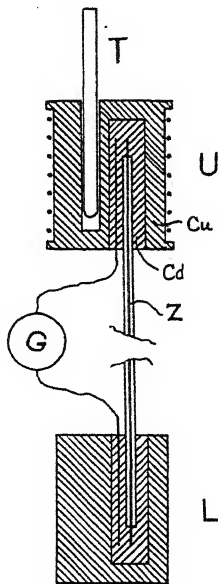


Fig. 1. Apparatus for measuring thermo-electric e.m.f.

If these curves could be represented in the usual manner by an equation of the form

$$E = AT + BT^2, \quad (1)$$

then  $E/T = A + BT$  and a straight line should be obtained by plotting  $E/T$  against the temperature difference  $T$ . The curves in Fig. 3, however, are not straight lines as this simple theory demands. Therefore, the thermo-electric power  $dE/dT$  is not a linear function of  $T$ .

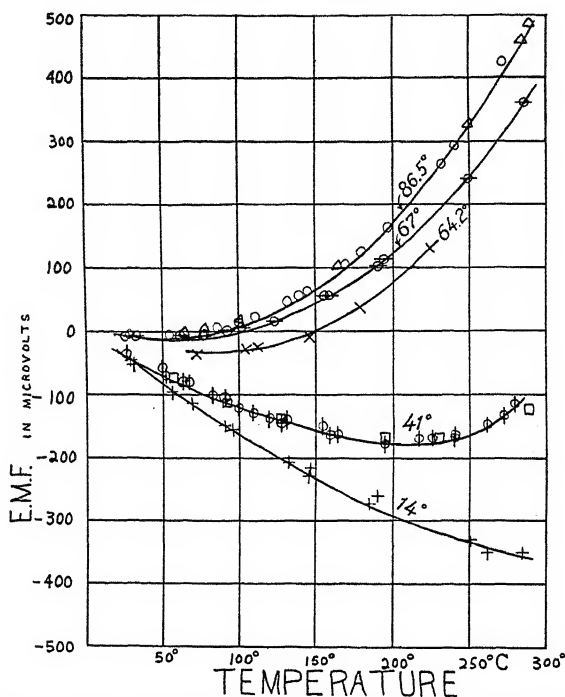


Fig. 2. E.m.f. vs temperature curves for different orientations.

The nature of the relationship between the curves of Fig. 2 can probably best be shown by plotting the neutral temperature against the orientation. The neutral temperature is defined as that temperature at which the thermo-electric power is zero. If we plot these values against the corresponding orientations we obtain the curve shown in Fig. 4. In the case of the curve for the 14° orientation, this neutral temperature was calculated by assuming the curve to be of the type represented by Eq. (1). This, of course, gives only a very rough value. No attempt will be made here to present a theoretical interpretation of these results, this being only a preliminary account of experimental work which is not yet completed.

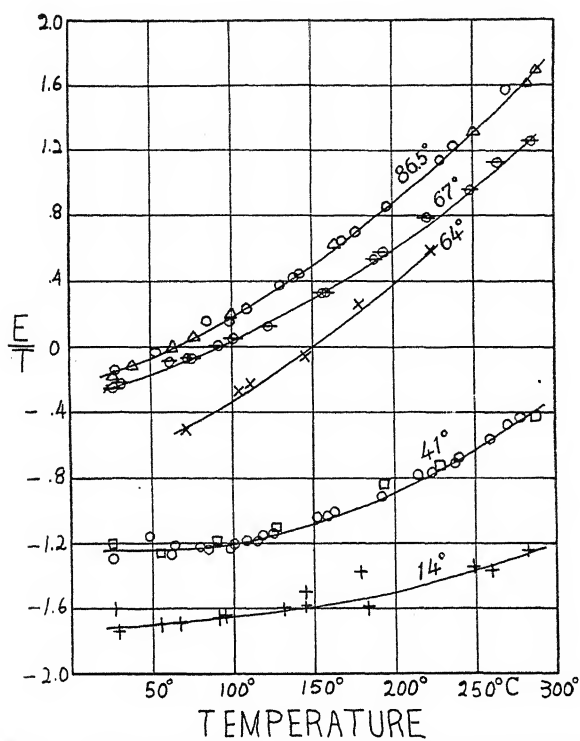


Fig. 3.  $E/T$  vs temperature curves for different orientations.

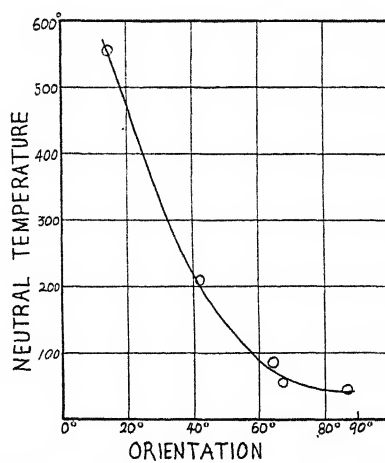


Fig. 4. Variation of neutral temperature with orientation.

In conclusion, the writer wishes to acknowledge his indebtedness to Dr. E. P. T. Tyndall, who suggested the problem, and whose assistance and guidance have been most valuable.

PHYSICAL LABORATORY,  
UNIVERSITY OF IOWA,  
July, 1925

# A TREATMENT OF RADIATION-PRESSURE AND GAS-PRESSURE AS DUE TO INTER-MOLECULAR FORCES

BY JOHN Q. STEWART

## ABSTRACT

(1) *Eddington's summation of gas-pressure and radiation-pressure.* The average repulsive force between two gas molecules associated with the emission of radiation by the one and its absorption by the other is calculated. Substitution of this value in the virial of Clausius justifies Eddington's proposition (in his theory of stellar constitution) that the total pressure is the sum of the gas-pressure and the radiation-pressure. (2) *The Boyle-Gay Lussac Law as a consequence of repulsive forces between molecules* is exhibited by an analogous treatment of gas-pressure, which ascribes it to similar inter-molecular forces. (Of course the hypothesis that such forces exist is merely a statistical fiction.)

## I. THE CONTRIBUTION OF RADIATION-PRESSURE TO TOTAL PRESSURE, CALCULATED FROM THE VIRIAL

IN Eddington's well-known theory of stellar constitution,<sup>1</sup> the total pressure (in the equations for gravitational equilibrium of a gas at high temperature) is taken as the sum of the gas-pressure and the radiation-pressure. While this proposition has appeared so plausible as to escape questioning, the following proof, employing the virial of Clausius (of the kinetic theory of gases), is of interest.

When there is a repulsive force,  $\phi(r)$ , between every two molecules of a gas, which is a function only of the distance  $r$  between them, the total pressure  $p$  is given, according to the theorem of Clausius,<sup>2</sup> by

$$pv = \frac{1}{3} \sum mV^2 + \frac{1}{3} \sum \sum r\phi(r). \quad (1)$$

Here  $v$  is the volume of the gas considered,  $m$  the mass and  $V$  the speed of any molecule. The summations are taken over all of the molecules in the volume  $v$ .

Let  $p_g$  represent gas-pressure, and  $p_r$  the radiation-pressure. For a perfect gas,

$$\frac{1}{3} \sum mV^2 = p_g v. \quad (2)$$

The assumption (justified in the sequel) may be made that (2) holds also

<sup>1</sup> A. S. Eddington, Monthly Notices of R. A. S.; Astrophysical J. **48**, 205 (1918).

<sup>2</sup> J. H. Jeans, The Dynamical Theory of Gases, 2nd ed., 1916, pp. 141-143.



when radiation-pressure is appreciable. Hence, Eddington's proposition, that

$$p = p_g + p_r, \quad (3)$$

will be confirmed if

$$\frac{1}{3} \sum \sum r \phi(r) = p_r v. \quad (4)$$

Accordingly, the next step in the proof is the evaluation of the  $\phi(r)$  appropriate for radiation-pressure in a gas at high temperature. (As the study is a statistical one, the divergence between the quantum and classical viewpoints does not enter into the problem.) Let  $Bd\Omega$  represent the quantity of radiant energy of all frequencies traveling in unit time across unit area within the gas, in the directions included within an elementary cone of solid angle  $d\Omega$  (with its vertex lying in the given area and its axis at right angles to it). If  $K$  is the coefficient of opacity, the quantity of energy taken up ("absorbed") in unit time by unit volume of the gas is  $4\pi KB$  (supposing  $B$  independent of direction). Assuming radiative equilibrium, this is the same as the quantity emitted (including that scattered).

If there are  $n$  molecules in unit volume, the quantity of radiant energy emitted (in all directions) in unit time per molecule is

$$E_0 = 4\pi KB/n. \quad (5)$$

This energy, owing to diversion ("absorption") by neighboring molecules as it flows outward, will at a distance  $r$  have been reduced to  $E$ , say; and the usual exponential formula for the reduction by opacity gives

$$E = E_0 \epsilon^{-Kr}, \quad (6)$$

where  $\epsilon$  is the base of natural logarithms.

Thus, at distance  $r$  from a given molecule, the quantity of radiant energy flowing outward, in the directions included within an elementary cone of solid angle  $d\Omega$  (with its vertex at the molecule) is  $Ed\Omega/4\pi$  per unit time. From the spherical shell of radii  $r$  and  $(r+dr)$  this cone intersects the volume  $r^2 d\Omega dr$ , which contains  $nr^2 d\Omega dr$  molecules. In unit time these take up, from the radiant energy flowing out from the central molecule, the quantity of energy  $KE dr d\Omega/4\pi$ .

Thus, each of the molecules at distance  $r$  diverts in unit time radiant energy emitted from the central molecule amounting to  $KE/4\pi nr^2$ . This energy is associated with outward momentum  $KE/4\pi cnr^2$  c.g.s. units, where  $c$  is the speed of light.

Accordingly, making the substitutions indicated in (6) and (5), the (statistical) force of repulsion correlated with radiation pressure between

two molecules at distance  $r$  is

$$\phi(r) = \left(\frac{B}{c}\right) \frac{K^2}{n^2 r^2} e^{-Kr}. \quad (7)$$

For a given molecule—referring to (1)—, supposing the dimensions of the volume  $v$  rather large in comparison with  $1/K$ ,

$$\sum r\phi(r) = \int_0^\infty 4\pi n r^3 \phi(r) dr = \frac{4\pi K^2 B}{cn} \int_0^\infty r e^{-Kr} dr = \frac{4\pi B}{cn}. \quad (8)$$

Furthermore,

$$\sum \sum r\phi(r) = nv \sum r\phi(r) = 4\pi Bv/c. \quad (9)$$

The radiation-pressure, on the other hand, is given by

$$p_r = (4\pi B/c) \int_0^{\pi/2} \sin^2\theta \cos\theta d\theta = 4\pi B/3c. \quad (10)$$

A comparison of (9) and (10) confirms (4), and hence (3).

If the absolute temperature is  $T$ , Stefan's law gives for the radiant energy in unit volume,

$$4\pi B/c = aT^4, \quad (11)$$

where  $a$  is a universal constant.

## II. AN EXPLANATION OF GAS-PRESSURE AS DUE TO REPULSIVE FORCES BETWEEN MOLECULES

According to the kinetic theory, gas-pressure is due to the motion of molecules. This conclusion, of course, has been established beyond all doubt; but the treatment of radiation-pressure just given suggests an alternative treatment of gas-pressure which substitutes for molecular collisions a statistical (but fictitious) force of repulsion between molecules, analogous to that described in (7) above.

It is readily shown from (1) that the Boyle-Gay Lussac law—namely

$$p_g = nRT, \quad (12)$$

where  $R$  is the gas-constant per molecule—will be satisfied if the molecular velocities are all zero and there is a force of repulsion between every two molecules at distance  $r$ , given by

$$\phi(r) = \left(\frac{3nRT}{4\pi}\right) \frac{k^2}{n^2 r^2} e^{-kr}, \quad (13)$$

where  $k$  is independent of  $r$ .

It has been stated<sup>3</sup> that it is impossible to explain gas-pressure as due

<sup>3</sup> J. H. Jeans, loc. cit.<sup>2</sup>, pp. 143, 144.

to inter-molecular repulsive forces; doubtless such statements do not contemplate the inclusion of  $n$ , the number of molecules in unit volume, in the formula for  $\phi(r)$ .

Further inquiry into the analogy between (13) and (7) suggests that  $k$  should be interpreted as the reciprocal of the molecular free path. In an approximate treatment, the molecules may be supposed each to have the same speed  $C$ , and the same kinetic energy  $\frac{1}{2}mC^2 = \frac{3}{2}RT$ . Thus the momentum of each molecule is

$$mC = 3RT/C. \quad (14)$$

Writing  $k$  for the reciprocal of the mean free path, other molecules make with a given molecule  $kC$  collisions in unit time, each of which diverts momentum  $3RT/C$ . Of these collisions, the fraction  $k\epsilon^{-kr}dr$  are with molecules which have traveled a distance between  $r$  and  $(r+dr)$  since their last previous collisions. But, in the spherical shell of radii  $r$ ,  $(r+dr)$ , surrounding the given molecule there are in all  $4\pi nr^2dr$  molecules. Hence, on the average, each of these contributes (through collisions with the given molecule) in unit time, the momentum,

$$\phi(r) = \left( \frac{3nRT}{4\pi} \right) \frac{k^2}{n^2r^2} \epsilon^{-kr}.$$

Thus (13) is justified as a statistical representation of the result given by kinetic theory.

PRINCETON UNIVERSITY OBSERVATORY,  
July 23, 1925

## ON THE SCATTERING OF LIGHT IN MIXTURES OF AIR AND CARBON DIOXIDE

BY DURGADAS BANERJI

## ABSTRACT

A beam of sunlight was focussed in a tube containing the mixture, and the intensity of the transversely scattered light was determined by comparison with a piece of blotting paper illuminated by diffuse light from the same beam, of which the intensity was varied by means of an iris diaphragm. The intensity varies linearly with the percentage of  $\text{CO}_2$ . By using a nicol, the ratio of the intensities of the components polarized in horizontal and vertical planes was found to vary in accord with the theory of scattering by mixtures of anisotropic molecules as developed by Raman.

## 1. INTENSITY OF SCATTERING IN GASEOUS MIXTURES

FOR a quantitative measurement of the transverse scattering of a mixture of gases two points must be particularly attended to: (1) The constituents must be thoroughly mixed before measurements of intensity are made and (2) the standard used in the visual photo-

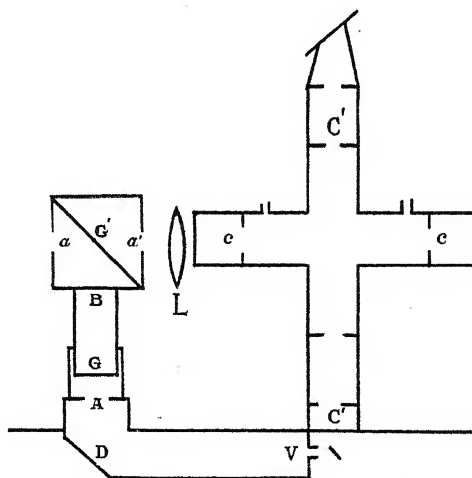


Fig. 1. Visual photometric arrangement for measuring intensity of scattered light.

metry should be such that it varies proportionately with any alterations in the intensity of the illuminating beam passing through the mixture. The following experimental arrangement was therefore adopted (Fig. I).

Sunlight reflected from a mirror and concentrated by the 18 cm objective of an astronomical telescope was allowed to pass through the

circular apertures  $a$  and  $a'$ , 3 cm in diameter, bored in a cubical wooden box, and was focused by a lens  $L$  at the center of the cross tube containing the mixture under examination. The beam of light was partially reflected to one side from a glass plate  $G'$  held diagonally inside the box, and after transmission through a blue glass plate  $B$  was allowed to fall on a ground glass screen  $G$ . The light from the ground glass passed through the adjustable aperture of an iris diaphragm  $A$  (the diameter being variable from  $1/16''$  to  $1''$ ) and fell on a diffusing screen  $D$ , made of white blotting paper held at an angle of  $45^\circ$ . The diffused light from this screen, after passing through a fine vertical slit  $V$ , fell directly on a slip of white blotting paper held vertically and turned so as to reflect the light passing through the slit in the direction  $CC'$  of the observer's eye. The whole apparatus was blackened inside so as to avoid errors due to stray illumination.

The cross tube employed to hold the mixture of gases was made of zinc sheet, with arms at right angles and each about 20 cm long, the ends being closed with clear glass windows, cemented on except the end opposite to that through which observations are made. To this was cemented a black bottle from which the bottom had been cut and to the mouth of which was cemented a black glass plate at an angle of  $45^\circ$ , thus securing an absolute blackness of the back ground against which the tracks are viewed. The inside of the cross tube is also blackened, and circular stops placed at intervals to cut off all stray illumination.

The scattered light from the center of the cross tube  $CCC'C'$ , can be seen inside a dark chamber as a horizontal blue patch, and the portion of the comparison photometer  $ADV$  being fixed on the inside wall of the chamber, the comparison standard can be seen as a blue colored slit of comparable intensity, but with a slight parallax between the two. The position of the observer's eye being at a definite distance, the two have the appearance of a T lying on its side, of which one part can be varied to obtain equality of brightness by adjusting the aperture of the iris diaphragm. Preliminary tests showed that the brightness of the variable standard was proportionate to the area of the aperture. The range of adjustment was sufficient to match the comparatively feeble scattering of air on the one side, and the stronger scattering due to carbon dioxide on the other.

To fill the cross tube with the sample to be examined, the tube was at first exhausted of air by means of an auxiliary pump, and carbon dioxide from the cylinder and air, made dust-free by passing through a sufficient layer of cotton wool, were admitted, one after the other, through the side tube so as to make up the desired mixture. The pro-

portion of carbon-dioxide and air could be regulated by indications of a manometer fitted to the exhaust circuit, and the sample, being thoroughly mixed by standing a sufficient length of time (generally an hour), could be submitted to chemical analysis by tapping out a portion in a 50 cc burette with a stopcock kept inverted over mercury and suitably connected to a branch of the exhaust circuit. The volumetric proportion in the sample was estimated quite accurately by absorption of carbon dioxide by a solution of caustic potash. The thoroughness of mixing was proved by the agreement of the indications of the manometer with the volumetric analysis.

The observed values of the intensity of the transversely scattered light are plotted against the percentage volume of carbon dioxide in Fig. 2. It will be noticed that the variation of intensity of the transversely scattered light with composition is linear.

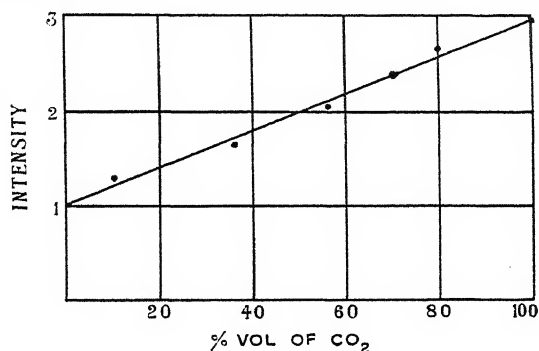


Fig. 2. Intensity of transversely scattered light as a function of percentage of CO<sub>2</sub>.

## 2. STUDY OF THE IMPERFECTION OF POLARIZATION OF THE SCATTERING

In order to make quantitative measurements of the imperfection of polarization a double image prism and a nicol rotating at the center of a graduated circle were used. The double image prism placed in front of the observation end of the cross tube, was adjusted to give two images of the aperture illuminated by scattered light, polarized respectively in vertical and horizontal planes. As the nicol was rotated behind the prism, two positions could be found for which the images were of equal brightness. If  $2\theta$  be the angle between the two positions of the nicol, the ratio of intensities of the two components is given by  $\tan^2\theta$ . The observations were made inside the dark chamber, the nicol being fitted to its wall.

The values of  $100\rho$ , where  $\rho$  is the ratio of the intensity of the vertical to the horizontal component of the polarized scattered light, have been

plotted against the percentage volume of carbon-dioxide in the mixture, in Fig. 3. It will be observed that the ratio increases rapidly at first and afterwards more slowly with the gradual increase of the amount

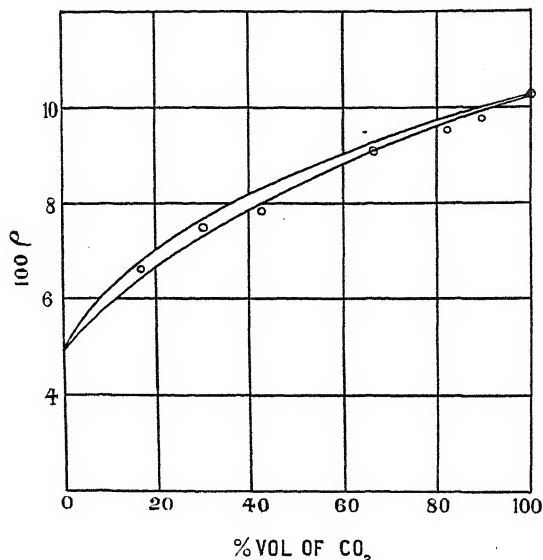


Fig. 3. Ratio ( $\times 100$ ) of horizontal to vertical components of polarization.

of carbon dioxide in the mixture. The fact has received a satisfactory theoretical explanation as indicated in the next section.

#### COMPARISON WITH THEORY

The theory of light-scattering in gaseous mixtures with anisotropic molecules may be approached from two different points of view which give identical results so long as the density of the mixture is not so great as to cause any appreciable deviation from the perfect gas laws. The first method is, following Rayleigh, to regard the individual molecules through which the primary waves of light pass as independent scattering centers and consider their effects as additive. The second method is to follow the general theory for fluid mixtures with anisotropic molecules as developed by Raman and Ramanathan.<sup>1</sup> In this theory, three distinct effects are considered, namely, the scattering of light due to local fluctuations (1) of density and (2) of composition of the mixture, and (3) the scattering due to anisotropy of the molecules and their varying orientation. The sum of the density and composition scatterings in a mixture obeying the gas laws, is given by  $n_1 A_1 + n_2 A_2$

<sup>1</sup> Raman and Ramanathan, *Phil. Mag.* (Jan. 1923) p. 213.



where  $A_1$  and  $A_2$  are characteristic of each kind of molecule and are proportional to the square of their refractivities, and  $n_1$  and  $n_2$  are the number of each kind in unit volume.

The orientation scattering consists in the main of the unpolarized light to which each molecule contributes. The effect is the same in both the horizontal and vertical directions of vibration, in each case being equal to  $2B_1n_1 + 2B_2n_2$  where  $B_1$  and  $B_2$  are characteristic of each kind of molecule. In addition to this, we have also a small polarized part of the orientation scattering which appears only in the vertical component, and is  $1/13$ th part of the whole. Thus in a mixture of gases the total intensity of transversely scattered light is given by

$$I = (13/3)n_1B_1 + (13/3)n_2B_2 + n_1A_1 + n_2A_2$$

and the ratio of horizontal to vertical component of polarization by

$$\rho = \frac{2n_1B_1 + 2n_2B_2}{n_1A_1 + (7/3)n_1B_1 + n_2A_2 + (7/3)n_2B_2}$$

Knowing the values of  $\rho$  and  $I$  for the cases in which the one component or the other is alone present, both  $I$  and  $\rho$  for any composition of the mixture can be calculated. It is seen that  $I$  varies linearly with the composition, whereas  $\rho$  appears as the quotient of two terms and does not therefore vary linearly. The calculated results given by the smooth curves, in Figs. 2 and 3, were obtained from the formula given. In the experiments we are really dealing with a mixture of three gases, namely  $\text{CO}_2$ ,  $\text{O}_2$  and  $\text{N}_2$ , but as the proportion of  $\text{O}_2$  and  $\text{N}_2$  is not varied, the results indicated by theory are the same as for a binary mixture.

In conclusion the author wishes to express his thanks to Prof. C. V. Raman for his interest in the work and for his valuable suggestions.

210 BOWBAZAR STREET,  
CALCUTTA, INDIA,  
May 14, 1925.

## SIMULTANEOUS HIGH FREQUENCY AND DIRECT CURRENT RESISTANCES OF FINE WIRES AT VARIOUS TEMPERATURES

By J. D. STRANATHAN

### ABSTRACT

Simultaneous measurements of high frequency ( $3.12 \times 10^6$  cycles) resistance and d.c. resistance of platinum wires 0.0513 mm in diameter were made at temperatures ranging from about  $20^\circ$  to around  $750^\circ$  C. Such measurements were made by sending both a high frequency alternating current and a direct current through the wire and making simultaneous and independent measurements of alternating current, alternating potential drop, direct current, and direct potential drop. These measurements were made independent through proper use of choke coils and blocking condensers. For wires of this size no account need be taken of inductive reactance to a frequency of  $10^6$  cycles. The temperature of the wire was governed by the magnitudes of the currents through it. Such measurements were made on wires in air, in vacuum, and in  $H_2$  at atmospheric pressure. In all cases the high frequency resistance agreed with the d.c. resistance at all temperatures within the limits of error,  $\pm 1$  percent. The absorption of  $H_2$  by the platinum affected both resistances equally at the frequency used.

### INTRODUCTION

THE purpose of this work was twofold. According to theory the a.c. resistance for wires of the size used should be practically equal to the d.c. resistance, for frequencies up to the order of  $10^6$ . The numerous theoretical formulas, such as those of Kelvin,<sup>1</sup> Rayleigh,<sup>2</sup> and Russell,<sup>3</sup> giving the ratio between high frequency resistance and d.c. resistance have been verified by numerous experimenters working at normal temperatures. As far as the writer knows, there have been practically no such measurements at high temperatures; neither have any such measurements been made simultaneously. The purpose of the work reported in this paper was to develop a method for making such simultaneous measurements at any temperature desired and thus check theory with experiment.

A second purpose, to which the work of this paper is incidental, is to determine whether the absorption of gases by metals affects the high frequency resistance and the d.c. resistance equally. There has been some

<sup>1</sup> Lord Kelvin, Math. and Phys. Papers, 3, 491 (1890).

<sup>2</sup> Lord Rayleigh, Phil. Mag. 21, 381 (1886).

<sup>3</sup> A. Russell, Phil. Mag. 17, 524 (1909).

evidence<sup>4</sup> that the effects are not equal in the case of copper wires. Before a reliable study could be made of these effects it was necessary to develop some such method of simultaneous resistance measurements as herein outlined. Having now developed the method, it is the writer's intention to proceed to a thorough investigation of the relative effects of absorbed gases on the high frequency resistance and the d.c. resistance of various metals. Some data presented in this paper show that the absorption of  $H_2$  by platinum affects both resistances equally at the frequency used.

#### METHOD AND APPARATUS

The general method followed in getting simultaneous measurements of high frequency resistance and d.c. resistance was to send both high frequency alternating current and direct current through the test wire and make simultaneous and independent measurements of alternating current, alternating potential drop, direct current, and direct potential drop. The test wires chosen were of such size (platinum, 0.0513 mm in diameter) that theoretically (1) the high frequency resistance should be equal to the d.c. resistance, and (2) the inductive reactance at any frequency below  $10^6$  should be negligible as compared to the resistance. The negligible inductive reactance means that the impedance of the test wire, which can be calculated directly from the alternating current and the alternating potential drop, is practically equal to the a.c. resistance.

Fig. 1 shows the arrangement of apparatus. Currents, both alternating and direct, were sent through the test wire  $W$  by means of leads  $a$  and  $b$ . Potential drops, both alternating and direct, were measured across points  $c$  and  $d$ . Direct current was furnished by the storage battery  $B$  and measured by a Siemens-Halske ammeter  $I_{dc}$ . None of this direct current could be shunted around the test wire by the oscillator circuit because of the  $1\mu f$  blocking condenser  $C_2$ ; none could be shunted through the electrometer  $V_{ac}$  because of  $\frac{1}{2}\mu f$  blocking condensers  $C$ . The direct potential drop was measured by a high resistance ( $333\frac{1}{3}$  ohms per volt) Siemens-Halske voltmeter  $V_{dc}$ . The resistance of choke coils  $L$  was negligible as compared with the voltmeter resistance; hence, the voltmeter gave the true potential across points  $c, d$ . Under some conditions, however, the voltmeter did draw an appreciable part of the indicated current  $I_{dc}$ . The true current through the test wire was obtained by subtracting from  $I_{dc}$  the calculated current shunted by the voltmeter. Alternating current of the frequency desired was furnished by a vacuum tube oscillator to points  $e, f$ . The alternating current was measured by a Weston thermocouple ammeter  $I_{ac}$ . No direct current could pass through this meter because of the

<sup>4</sup> Austin Bailey, Phys. Rev. 20, 154 (1922).

$1\mu\text{f}$  condenser  $C_1$ ; the direct current was shunted around the meter by  $L_1$ . No appreciable high frequency current could be shunted around the ammeter  $I_{ac}$  by the battery circuit or by the shunt  $L_1$  because of the sufficiently high inductance of choke coils  $L_2$  and  $L_1$ . Likewise, no appreciable high frequency current could be shunted around the test wire by the d.c. voltmeter because of similar choke coils  $L$ ; neither could any be shunted through the high impedance electrometer circuit. The indicated high frequency current  $I_{ac}$  was then the current through the test wire. The alternating potential drop was measured by a Dolazalek electrometer  $V_{ac}$ , used idiostatically. The  $\frac{1}{2}\mu\text{f}$  condensers  $C$  kept direct potential from this electrometer, while a  $\frac{1}{2}$  megohm resistance  $R$  shunted across the electrometer vanes kept the reading free from fixed induced charges.

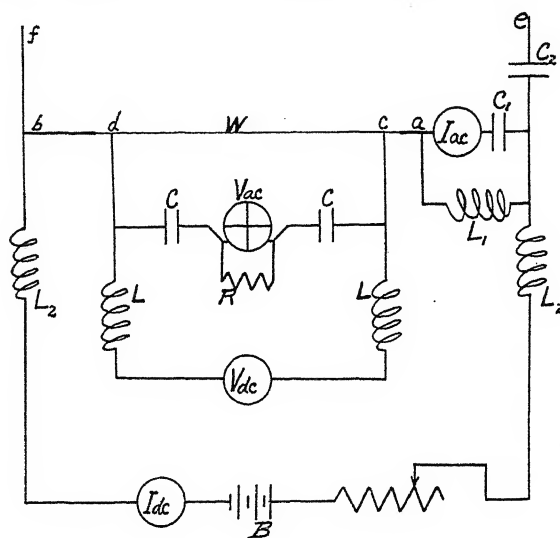


Fig. 1. Diagram of arrangement of apparatus.

Thus the electrometer indicated only the alternating potential drop, and this independently of the direct potential across the wire. Because the impedance of condensers  $C$  was negligible as compared to the impedance of the electrometer with its shunt  $R$ , the electrometer indication gave the true potential drop across points  $c, d$ .

Care was exercised in the relative placing of the parts of the apparatus. Anyone familiar with high frequency measurements appreciates the necessity of this. The test wire was kept as far as practical from other parts of the circuit in order to reduce its distributed capacity. Should there be a large distributed capacity between it and other parts of the circuit the high frequency current would not be uniform throughout

the length of the wire, and the thermo-ammeter would not indicate the true current through the wire. Such capacity currents were very small in this test, as shown by placing the thermo-ammeter first at one end of the test wire and then at the other; with oscillator conditions the same, no difference in indicated current could be observed.

In order to study the resistance of the test wire in a vacuum and in the presence of gases other than air, the wire was mounted as shown in Fig. 2. Electrical connections were made by means of wires run through rubber corks placed in the ends of a large glass tube. Through one cork was a glass tube for connection to the pumping system; through the other cork was a similar tube for connection either to a gauge or to an  $H_2$  tank. Mercury seals were placed around the corks at both the upper and the lower ends of the glass container. Small pieces of glass tubing were slipped over the potential leads and far enough into the corks to prevent electrical connection of leads *a* and *c* (and *b* and *d*) through the mercury. These glass tubes were filled with mercury for sealing.

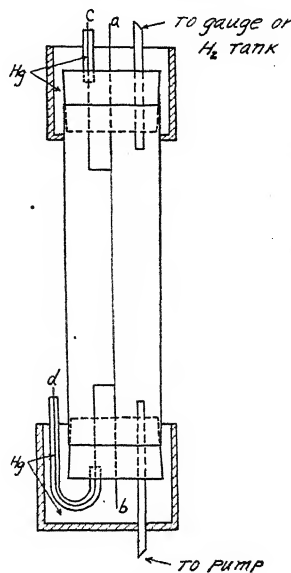


Fig. 2. Mounting of test wire

#### EXPERIMENTAL DATA AND RESULTS

In taking data, small currents were first sent through the test wire and readings of the various instruments recorded. With only small currents, the temperature of the test wire was not far different from that of the room. The currents through the wire were then increased gradually, readings being taken at frequent intervals, until the test wire was at a red heat. Sometimes the high frequency current was left small and the heating was done mainly by the direct current, while at other times the direct current was left small and the heating was done mainly by the alternating current. Results were the same in either case. Table I shows a complete set of such data taken for a platinum wire in air; results calculated therefrom are also shown.

The symbols heading the columns are for the most part self-explanatory.  $I'_{dc}$  is the actual direct current through the test wire, equal to  $I_{dc}$  minus the current shunted by the d.c. voltmeter.  $I'_{ac}$  is the alternating current through the test wire, equal to  $I_{ac}$  except for a calibration correction.  $V'_{or}$  is the net deflection of the electrometer and  $V_{ac}$  the corre-

sponding alternating potential drop as taken from the calibration curve of Fig. 3.  $R_{dc}$  and  $R_{ac}$  are the d.c. and a.c. resistances, respectively; the last column gives the percent difference in these two resistances.

TABLE I

*Data for platinum wire in air at atmospheric pressure*  
Pt wire No. 1, 0.0513 mm in diam., 78.9 cm long; frequency,  $3.12 \times 10^5$ .

$I'_{dc}$	$V_{dc}$	$R_{dc}$	$I'_{ac}$	$V'_{or}$	$V_{ac}$	$R_{ac}$	$R_{dc} - R_{ac}$
.0773	3.12	40.4	.1217	4.3	4.96	40.8	-1.0%
.1466	6.44	43.9	.1217	5.1	5.40	44.4	-1.1
.203	9.95	49.0	.1241	6.5	6.10	49.2	-.4
.292	16.8	57.5	.1232	9.1	7.22	58.6	-1.9
.380	28.1	74.0	.1246	14.9	9.24	74.2	-.3
.431	37.3	86.5	.1233	19.5	10.57	85.7	.9
.466	44.4	95.3*	.1250	24.4	11.87	95.0	.3
.480	47.2	98.3	.1250	25.9	12.25	98.0	.3
.490	49.9	101.8	.1261	28.1	12.78	101.3	.5
.491	50.4	102.6	.1276	29.4	13.06	102.3	.3

\* Test wire dull red. This symbol has the same meaning in following tables, also.

The electrometer was calibrated three times. Points for the various calibrations are indicated on the curve. These calibrations were made at 60 cycles with the condensers  $C$  omitted. Omission of these condensers is permissible since the potential drop across them at the frequency used in the test proper is negligible.

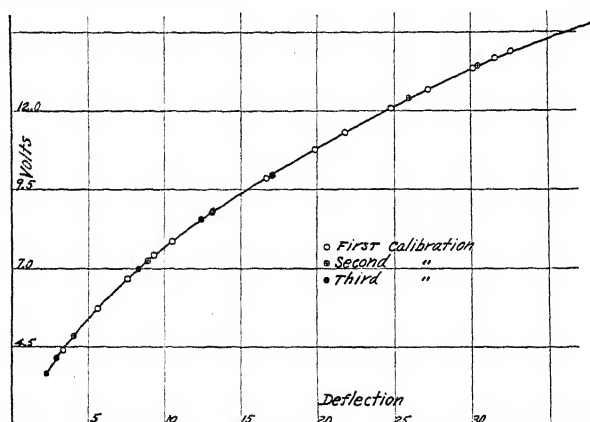


Fig. 3. Calibration of Electrometer.

Table II shows the results on the same platinum wire as previously used, when studied in vacuum at a pressure of the order of 0.05 mm Hg; the frequency was  $3.12 \times 10^5$  as before.

It will be noticed that the lowest resistance measured in vacuum is considerably higher than that in air. This is due to the higher temperature

produced by the small heating currents when in vacuum; the cooling due to convection currents in air is now absent.

One set of data was taken at a considerably higher frequency,  $6.34 \times 10^5$  cycles, on this same platinum wire in air. The results showed equally good agreement.

TABLE II  
*Data for platinum wire No. 1 in vacuum.*

$R_{dc}$	$R_{ac}$	Diff.	$R_{dc}$	$R_{ac}$	Diff.
60.3	60.4	-.2%	48.9	48.4	1.0%
74.2	74.7	-.7	69.2	69.5	-.4
92.4	91.7	-.8	91.1	91.3	-.2
103.2	103.8	-.6	102.6	102.0	.4
109.1*	109.3	-.2	116.8*	116.0	.7
119.9	118.9	.8	120.0	119.2	.7
121.1	119.9	1.0	60.2	59.3	1.5
			120.0	119.0	.8
			71.3	71.2	.1

Data taken with a second platinum wire of the same diameter, both in vacuum (0.01 mm Hg) and in air, showed similar results.

A third platinum wire of the same diameter was next studied in an  $H_2$  atmosphere. (Breakage prevented such a study on the first and second wires.) The glass tube container was exhausted with a mercury vapor pump for several hours, and the test wire repeatedly glowed red, such glowings sometimes lasting as much as 15 or 20 minutes. While the wire was being glowed in vacuum, electrolytically prepared  $H_2$  was let into the glass tube containing the test wire. The wire was repeatedly glowed in this, the  $H_2$  pumped out, and a fresh supply let in. Data were then taken while the wire was surrounded by  $H_2$  at atmospheric pressure, using a frequency of  $3.12 \times 10^5$  as before. Table III shows the results.

TABLE III  
*Data for Pt wire No. 3, in  $H_2$*

$R_{dc}$	$R_{ac}$	Diff.
38.7	39.5	-2.1%
39.3	39.8	-1.3
42.1	42.7	-1.4
47.9	48.4	-1.0
57.1	57.3	-.4
67.8	68.3	-.7
78.0	78.6	-.8
85.8	86.7	-1.0
99.6*	100.8	-1.2

The high frequency resistance seems to run consistently a little higher than the d.c. resistance, but a real difference is doubtful. If the absorption of  $H_2$  does affect the high frequency resistance and the d.c. resistance



differently, then the difference is certainly very small at the frequency used. No data with this wire in air were secured because of breakage.

A fourth platinum wire of the same diameter as those previously used was then studied, both in air at atmospheric pressure and in  $H_2$ . Its treatment with  $H_2$  was similar to that outlined for the third wire. Table IV shows the results at a frequency of  $3.12 \times 10^5$ . The test wire broke before getting red during the test in  $H_2$ .

TABLE IV  
*Data for Pt wire No. 4, both in air and in hydrogen.*

$R_{dc}$	In air $R_{ac}$	Diff.	$R_{dc}$	In hydrogen $R_{ac}$	Diff.
38.4	38.8	-1.0%	35.2	35.6	-1.1%
41.8	42.0	-.5	35.8	36.4	-1.7
52.8	52.8	.0	46.1	46.1	.0
76.0	75.4	.8	52.5	52.9	-.8
95.3*	94.4	.9	62.1	62.6	-.8
			72.0	72.6	-.8
			79.5	79.5	.0

Sufficient data have here been presented to prove the reliability and accuracy of the method. The accuracy is better than what should be expected in high frequency measurements. The application of the method to a thorough study of the effects of absorbed gases is now but a question of time.

#### SUMMARY

A new method has been developed for making simultaneous measurements of high frequency resistance and d.c. resistance of small wires at any temperature desired up to that at which the test wire will not support its own weight. The method is applicable up to any frequency limit for which the inductive reactance of the test wire is negligible as compared to the resistance; it is even applicable to higher frequencies provided proper account is taken of the reactance of the wire. The accuracy at these higher frequencies, however, is not so good.

The high frequency resistance (at  $3.12 \times 10^5$  cycles) of small platinum wires was found to be equal to the d.c. resistance at all temperatures, whether in air, in vacuum, or in an atmosphere of  $H_2$ .

BLAKE LABORATORY,  
UNIVERSITY OF KANSAS.  
June 15, 1925

# THE RELATION BETWEEN THE LOUDNESS OF A SOUND AND ITS PHYSICAL STIMULUS

BY J. C. STEINBERG

## ABSTRACT

Experiments with many types of sounds have shown that the loudness of a sound is a function of its energy frequency spectrum and its level above the threshold of hearing and that if this relationship be represented as follows:

$$L = \frac{10}{3} \log_{10} \left[ \sum_{i=1}^{i=k} (W_i P_i)^{2/r} \right] r^2$$

sounds whose calculated values  $L$  are equal will appear equally loud to the average normal ear.  $P_i$  is the r.m.s. pressure of the  $i$ th component of the sound wave. The weight and root factors  $W$  and  $r$ , respectively, are functions of the sensation level, which is synonymous with the term loudness as formerly used and is defined as follows:

$$S = 10 \log_{10} \left[ \sum_1^k P_i^2 / \sum_1^k P_{0i}^2 \right]$$

where  $P_{0i}$  is the r.m.s. pressure of the  $i$ th component when the complex sound is at the threshold of hearing. In case the components in a narrow band of frequencies  $\Delta n$  are not resolved their energy must be integrated to obtain the energy of the equivalent single component. The root factor  $r$  is inversely proportional to the ratio of the minimum perceptible increase in energy to the total energy. For intensities near the threshold, the weight factors are equal to the reciprocals of the minimum audible pressures. Curves are given showing the values of  $W$  for various frequencies at various sensation levels, also the values of  $r$  as a function of  $S$ . As the intensity is increased the weight factors give greater weight to the lower frequencies; hence, even though the amplitude of the sound wave be increased without distortion, the ear will perceive both an increase and a distortion. This effect is due to the non-linearity of the ear.

## INTRODUCTION

IT has been customary to regard sensation as being proportional to the logarithm of the stimulus. In the case of sound the stimulus is usually regarded as the amplitude of the pressure wave and the sensation refers to the loudness of the sound. Now, any relation between loudness and stimulus must be such that equal stimuli will appear equally loud to the average normal ear. Various experiments upon the loudness of sounds have shown that the simple relation stated above will not fulfill this condition, but that it is necessary to take a *function* of the amplitude as the stimulus.

The purpose of this paper is to formulate tentatively such a function and to determine the various factors that enter into the expression from the experimental data that is now available. Most of these data

were taken for other purposes so that in some cases it will appear that the factors could have been obtained from more direct experiments. However, until such data are obtained it is worth while to make the most of the existing data.

*Loudness* is defined on an arbitrary scale such that sounds having the same numerical value on this scale are judged to be equally loud by the average normal ear. It is found to depend on both the sensation level and the pressure spectrum. By *sensation level* is meant the number of units that the amplitude of any sound wave must be reduced in order to reach the threshold, which in the past has been variously referred to as loudness level, volume, or intensity, and is defined as follows:

$$S = 20 \log_{10}(P/P_0) \quad (1)$$

where  $P$  is the pressure of the sound wave and  $P_0$  the minimum audible pressure for an average normal ear, both being expressed as root mean square values. The sensation level of any sound is then the number of TU that the amplitude must be reduced to reach the threshold of audibility.<sup>1</sup> The ear will accommodate about 100 TU. Ordinary conversation is usually carried on at sensation levels between 60 and 80 TU.

It was found convenient in defining loudness to fix the numerical value of the scale so that the calculated loudness of a 700 cycle tone is approximately equal to its sensation level when the level is greater than 60 TU which covers the range of practical levels. The equality does not hold at the lower levels and could not be made to do so without greatly complicating the method. As stated above, the loudness depends in general not only upon the sensation level but also upon the frequency, if it is a pure tone, or upon the pressure spectrum if it is complex.

The *pressure spectrum* that is dealt with here is that which would be produced in the ear canal if the walls and drum were rigid.<sup>2</sup>

In a former paper<sup>3</sup> data were given on the loss in the resultant loudness of a complex sound when the energy was removed from a particular frequency range of the sound. This loss was measured by observing the fractional amount of the initial energy that was required to make it sound equally loud to the remaining portion of the initial spectrum. Hence, loudness in the former use is equivalent to the present sensation

<sup>1</sup> See transmission unit and telephone transmission reference system by W. H. Martin, Bell. Tech. Jour. 3, 400 (July, 1924) and A. I. E. E. Jour. 43, 504 (June, 1924).

<sup>2</sup> Inasmuch as it is difficult to determine the spectrum that actually exists in the immediate neighborhood of the ear drum, it seemed much more desirable to deal with the above spectrum. It will be seen from the manner in which the equation has been formulated that this procedure is legitimate.

<sup>3</sup> H. Fletcher and J. C. Steinberg, Phys. Rev. 24, 306 (Sept., 1924).

level and should be distinguished from loudness as defined above. An empirical method was developed for calculating these fractional losses for several types of complex sounds. It is evident that these losses do not give a true indication of the amount by which the loudness (as used here) has been decreased, because the relation between the energy of the initial spectrum and its loudness was not known. Although the method that was developed has an important application to problems in telephone engineering, it was desirable to deal with loudness in the more general way. As will be seen later, the earlier formula is a special case of the more general relation.

#### FORMULATION OF THE LOUDNESS FUNCTION

The type of function that is necessary in order to represent the relation between the loudness of a sound, the amplitude of the sound wave and the sensation level, was suggested by various experimental data. The formulation of this function will be made on the basis of general conclusions drawn from a study of these data. It is necessary to distinguish between sounds having "discrete frequency components" and those having the so-called "continuous energy frequency spectrum." The statements that follow apply to a sound of the first type whose components are separated by an interval of 60 or more cycles. Modifications appropriate to the other types of spectrums will be discussed in a later paragraph.

The experiments in the paper referred to above indicated that within the error of making the measurements *the contribution of each frequency region to the resultant loudness could be obtained by summing a root of the weighted energy in each frequency region.* The weight factors depended upon the frequency of the region in question and upon the sensation level of the sound. The root depended only upon the sensation level. Hence, a summation of the type

$$\sum_{i=1}^{i=k} (W_i P_i)^{2/r} \quad (2)$$

is used in adding together the contributions of the individual components.<sup>4</sup>

It has been found from observations on the loudness of complex sounds near threshold that when the component pressures have values less than the values required for them to be audible when heard alone, they do not contribute to the loudness. Rather than take care of this discontinuity

<sup>4</sup> The weight factor in Eq. (2) is not the same as the weight factor that was used in the former paper. Their relation will be given later on.

by means of the weight factors it is more convenient to extend the summation of Eq. (2) *only over those components whose pressures are greater than their respective minimum audible pressures when heard alone.*

There is much evidence which indicates that the mechanical members transmitting the pressure wave from the ear drum to the cochlea fail to obey Hooke's law when the pressures are sufficiently great. Several attempts, based upon various assumptions, have been made to represent this state of affairs mathematically. Owing to uncertainties concerning these assumptions and also to lack of information as to the mechanical constants of the ear, the equations that have been obtained have little value in themselves and they will not be discussed here. They have, however, a common characteristic in that they all indicate that the degree in  $P$  of a functional relationship between loudness and pressure depends upon the intensity, and that the ratio of the degree at low intensities to that at high intensities is 3. Now, it was observed experimentally that the ratio of the values of  $r$  corresponding to approximately these same intensities was also 3. Hence, in order to satisfy this requirement as to the degree of the pressure, the following expression will be used

$$\left[ \sum_{i=1}^{i=k} (W_i P_i)^{2/r} \right]^{r^2}. \quad (3)$$

If we regard this as the physical stimulus, then in accordance with Fechner's law

$$L = K \log_{10} \left[ \sum_{i=1}^{i=k} (W_i P_i)^{2/r} \right]^{r^2}. \quad (4)$$

where  $L$  is the loudness,  $K$  is a constant which we are at liberty to choose,  $W_i$  is a weight factor which depends upon the frequency and the sensation level of the sound,  $P_i$  is the root mean square pressure of the  $i$ th component of the acoustic wave,  $r$  is a root factor that depends only upon the sensation level of the sound. The summation extends only over those components having pressures greater than their individual minimum audible pressures.

From the definition of sensation level it follows that  $P_i^2 = 10^{S/10} P_{0i}^2$  so that Eq. (4) may be written in the following form

$$L = K \log_{10} 10^{Sr/10} \left[ \sum_{i=1}^{i=k} (W_i P_{0i})^{2/r} \right]^{r^2} \quad (5)$$

where now  $P_{0i}$  is the r.m.s. pressure of the  $i$ th component when the complex sound is just audible and  $S$  is the sensation level of the sound in TU. This then is the equation sought which gives the relation between

loudness, the sensation level and the pressure spectrum. It remains now to determine the functional curves which give the value of  $W$  and  $r$  for various frequencies and sensation levels.

#### DETERMINATION OF THE WEIGHT AND ROOT FACTORS

When there is only one component. Eq. (4) becomes

$$L = K \log W^{2r} E^r \quad (6)$$

where  $P^2 = E$ . If we assume that  $W$  and  $r$  are sensibly constant for small changes in  $E$ ,

$$\delta L = kr \log_{10} e \cdot (\delta E/E). \quad (7)$$

If  $r$  were a constant, Eq. (7) would be the *Weber-Fechner law relating sensation with stimulus*. It is known, however, from the filter experiments

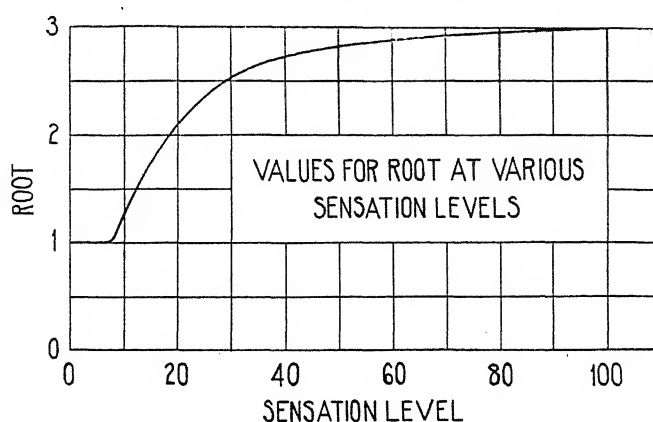


Fig. 1

that  $r$  is a function of  $S$  and that its upper limit (that is when  $S=100$ ) is 3. The filter experiments do not determine  $r$  uniquely at the lower levels although they indicate that  $r$  decreases as  $S$  decreases and becomes equal to 1 at sensation levels of about 10 TU. Knudsen<sup>5</sup> found that the minimum perceptible values of  $\delta E/E$  depended upon  $S$ . If  $\delta L$ , the least perceptible increment of loudness, is a constant, Eq. (7) predicts that the values of  $\delta E/E$  for the above levels would stand approximately in the ratio of 3. Knudsen's results show that this is the case. Hence, *two independent sets of experimental data are brought into accord* by the equation. Taking the upper limit of  $r$  equal to 3 the relation between  $S$  and  $r$  as shown on Fig. 1 was obtained from the experimental values of  $\delta E/E$  and Eq. (7). When the sensation level is less than 10 TU it is difficult to determine the value of  $r$  from these data. Other data indicate, however,

<sup>5</sup> V. O. Knudsen, Phys. Rev. 21, 84 (Jan. 1923).

that at these levels the response of the ear is substantially linear and that the individual components contribute in proportion to their energy so that  $r$  would have the value of unity.

It is desirable to have the loudness  $L$  as expressed by Eq. (6) equal to zero when the pressure  $P$  equals the minimum audible pressure. This can be done by taking  $W=1/P_0$  for  $S=0$ , where  $P_0$  is the minimum audible pressure for the tone. The set of weight factors for  $S=0$  which are shown on Fig. 2 were obtained in this manner from the sensitivity of normal ears at threshold.<sup>6</sup>

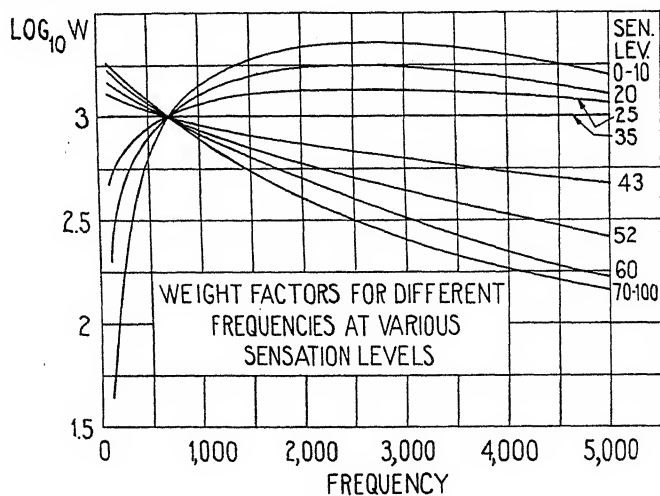


Fig. 2

When the sound is complex the condition to be satisfied at threshold is that

$$\sum_1^k (W_i P_i)^2 = 1. \quad (8)$$

This condition is satisfied by the above set of weight factors, for as  $S$  approaches 0, terms drop out of the summation until at  $S=0$  there is only one term left. This term has the minimum audible value of a pure tone of like frequency, hence, the summation is equal to unity at threshold.

If the components are less than 60 cycles apart or the spectrum is continuous, a difficulty arises because the ear does not resolve the components. Thus the complex sound may be audible when the components are separately inaudible. Let  $P_n^2$  be a function such that the  $\int_{n_1}^{n_2} P_n^2 dn$  is proportional to the energy contained in the range  $n_1$  to  $n_2$ . In order

<sup>6</sup> H. Fletcher and R. L. Wegel, Phys. Rev. 19, 553 (June, 1922);  
R. L. Wegel, Bell Tech. Jour. 1, 56 (Nov. 1922).



that the equation developed above be applicable to this type of sound, the energy in a narrow band of frequencies must be considered as equivalent to a single component in contributing to the total loudness. Thus,

$$P_i^2 = \int_{(n-\Delta n/2)}^{(n+\Delta n/2)} P_n^2 dn \quad (9)$$

where  $P_i$  is a component of frequency  $n$  which is equivalent to the integral in contributing to loudness. If we substitute Eq. (9) in Eq. (2) and regard  $W_n$  and  $P_n$  as practically constant for a small change  $\Delta n$ , the following relation can be obtained:

$$\sum_1^k (W_i P_i)^{2/r} = \int_0^n \frac{(\Delta n)^{1/r}}{\Delta n} W_n^{2/r} P_n^{2/r} dn. \quad (10)$$

The band width  $\Delta n$  is a fundamental property of the ear, and is no doubt different for the different frequency ranges of a given spectrum. When such a sound is at threshold this width is obviously determined by the following equation,

$$\int_{(n-\Delta n/2)}^{(n+\Delta n/2)} P_n^2 dn = P_0^2 \quad (11)$$

where  $P_0^2$  is the minimum audible pressure of a tone of frequency  $n$ . The frequency is determined by the last frequency region to become audible as the sound is reduced to threshold. If we assume that the effective band width is the same for the different frequency regions, Eq. (5) becomes for the case of the continuous spectrum,

$$L = \frac{10}{3} r^2 \log \frac{(\Delta n)^{1/r}}{\Delta n} \cdot 10^{S/10r} \int_0^n W_n^{2/r} P_{0n}^{2/r} dn \quad (12)$$

where  $P_{0n}$  is the value taken by  $P_n$  when the complex sound is at threshold. The limits of integration extend only over the band widths whose equivalent single tones have intensities greater than their individual minimum audible intensities. Hence, the integral of Eq. (12) satisfies the condition expressed by Eq. (8) for the same reasons as obtained for the summation.

It will be noticed in Fig. 1 that the value of  $r$  becomes constant when the sensation level is greater than 87 TU. This enabled the direct determination of the weight factors for levels greater than 87 TU from the observed fractional losses for speech at a level of 100 TU. When a part of the frequency range is removed by means of a high or a low-pass filter,

Eq. (12) remains unchanged except that the limits of integration include only the transmitted frequency range. If the sensation level of the original sound be decreased by an amount  $\bar{a}$ , in order that it be as loud as the filtered sound, the following equation is obtained:

$$K r^2 \log \frac{(\Delta n)^{1/r}}{\Delta n} 10^{(S-\bar{a})/10r} \int_0^\infty W_n^{2/r} P_{0n}^{2/r} dn = \\ K r^2 \log \frac{(\Delta n)^{1/r}}{\Delta n} \cdot 10^{S/10r} \int_0^C W_n^{2/r} P_{0n}^{2/r} dn. \quad (13)$$

where  $C$  is the cut-off frequency of a low-pass filter. Now the value of  $r$  in the left-hand member of Eq. (13) corresponds to the sensation level  $(S-\bar{a})$ , whereas the value in the right-hand member corresponds to the sensation level  $S$ . It was observed that  $\bar{a}$  was never greater than 15 TU so that for these experiments the value of  $r$  is the same at the two levels. Hence, Eq. (13) can be written in the form

$$10^{-\bar{a}/30} = \left[ \int_0^C W_n^{2/3} P_{0n}^{2/3} dn \right] / \left[ \int_0^\infty W_n^{2/3} P_{0n}^{2/3} dn \right] \quad (14)$$

$P_{0n}^2 dn$  is proportional to the energy in the frequency range  $(n+dn)$  to  $(n-dn)$  of undistorted speech. Measurements of this quantity have been made by Crandall and Mackenzie.<sup>7</sup>

In the earlier paper, the following empirical relation was obtained from the data on speech:<sup>8</sup>

$$10^{-\bar{a}/30} = \int_0^C G(n) dn \quad (15)$$

and the function  $G(n)$  was determined.

Equating Eqs. (14) and (15) we can write

$$W_n^{2/3} = \left[ G(n) \int_0^\infty W_n^{2/3} P_{0n}^{2/3} dn \right] / P_{0n}^{2/3}. \quad (16)$$

The integral in the numerator is independent of the frequency. Hence, the *relative* values of the weight factors for a level of 100 TU could be determined. Their absolute values were fixed by taking the value of  $W_n$  for a frequency of 700 cycles equal to its value at the sensation level of zero, for reasons that will appear later. The weight factors that were determined in this manner are shown in Fig. 2.

<sup>7</sup> I. B. Crandall and D. Mackenzie, Phys. Rev. 19, 221, (Mch. 1922).

<sup>8</sup> Loc. cit.<sup>3</sup> (see Eq. 9.  $G(n) = W^b$ ).

This set of factors together with the set obtained at the level of  $S=0$  give the limits between which the weight factors vary as the sensation level changes. The sets appropriate between these limits could not be determined in any such direct manner because  $r$  could not be taken as sensibly constant. They were determined by methods of successive approximation from the filter data on test tone and are shown in Fig. 2.

The arbitrary constant  $K$  was chosen so that the loudness of a 700-cycle tone would be approximately equal to its sensation level for most of the practical range. The weight factors for a tone of this frequency are constant and equal to the reciprocal of the minimum audible pressure. Hence, its loudness reduces to the following simple equation

$$L_{700} = KSr/10. \quad (17)$$

Now  $r$  is equal to 3 for most of the important sensation range so that if  $K$  is equal to  $10/3$ , the values of  $L_{700}$  and  $S$  will be numerically equal for this range. By giving  $K$  this value it is possible to determine the loudness of the sound by noting the sensation level of the 700-cycle when it is as loud as the sound in question.

#### THE CALCULATION OF LOUDNESS

The final form of the loudness equation is as follows:

$$L = (10/3)r^2 \log \sum_{i=1}^{i=k} (W_i P_i)^{2/r} \quad (18)$$

where  $W$  and  $r$  are defined by the curves shown in Figs. 1 and 2.

As stated in the beginning, in order to compute the loudness of the sound, it is necessary to know the pressure spectrum and the sensation level. It is clear from the manner in which the equation has been formulated that the pressure spectrum could be measured in any arbitrary way provided the measuring system is a linear one and the corresponding sets of weight factors determined on the basis of such measurements. Once the weight factors have been determined, it is then necessary to make all subsequent measurements in the same way. The pressure spectrum that has been used in obtaining the present set of weight factors was adopted because it enabled the direct use of measurements upon the sensitivity of normal ears,<sup>9</sup> and because it is not difficult to calibrate an electrical system so as to obtain such a spectrum.

The sensation level is most conveniently measured by means of a resistance network attenuator<sup>9</sup> that is calibrated to read the attenuation in transmission units. In this way the sensation level is measured directly.

<sup>9</sup> H. Fletcher and R. L. Wegel, *Phys. Rev.* **19**, 553 (June, 1922).

When the tone has sustained frequency components, its sensation level is equal to the maximum value of the sensation levels of the components. Hence, it is possible to calculate the sensation level of such tones from their pressure spectrums.

It is not feasible to make a direct determination of the loudness of a sound by simply listening to it. Although loudness can be determined directly by using a 700-cycle tone as a comparison tone when the loudness is greater than 70 units, extensive measurements of this kind have not been made. The equation finds its greatest usefulness in enabling us to calculate how much the sensation level of one sound must be changed in order that it be equally loud to some other sound. In this way the equation has been checked indirectly by experiments upon a wide variety of complex sounds. The calculated and observed results will be given for a few representative cases.

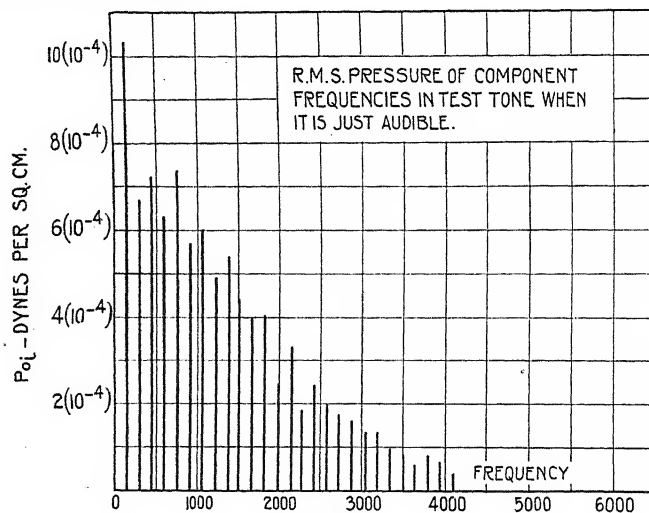


Fig. 3

A case of interest is the loss caused by removing a portion of the frequency range from a complex sound. The loss was measured by reducing the sensation level of the original sound until it was as loud as the filtered sound. In order to calculate this loss, the loudness  $L$  of the initial sound at various values of the sensation level was computed from Eq. (17). Thus, a curve giving  $L$  in terms of  $S$  was obtained for the initial sound. The loudness  $L'$  was then computed for the filtered sound. The amount  $\bar{a}$  by which the initial sound must be attenuated in order that  $L = L'$  was obtained graphically from the  $L$  vs  $S$  curve.

Figs. 3 to 5 give the results for a tone having sustained frequency components which is designated as "test tone." The pressure spectrum

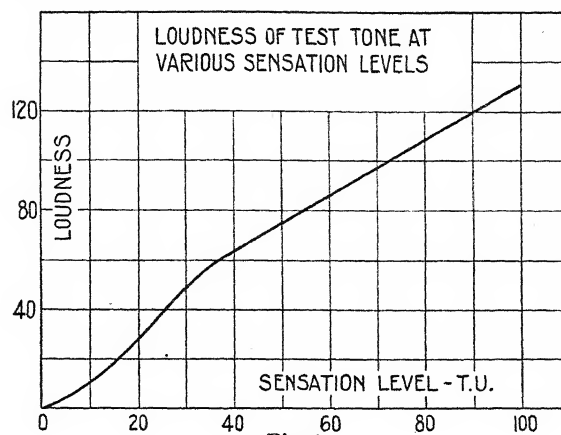


Fig. 4

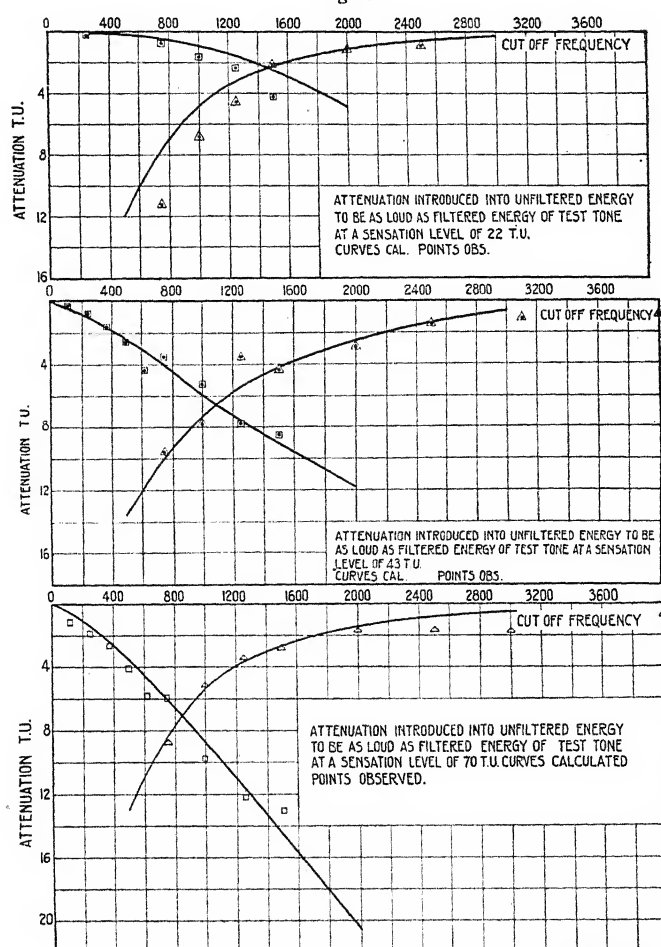


Fig. 5

was obtained from a Fourier analysis of the voltage impressed upon a calibrated receiver. From the pressure spectrum the loudness was computed at various sensation levels (Fig. 4). When the level of the initial tone is 70 TU its loudness is 97 units. When all the frequencies below 1000 cycles were eliminated, the computed loudness was 83 units. It will be seen from Fig. 4 that the sensation level must be reduced 9 TU below

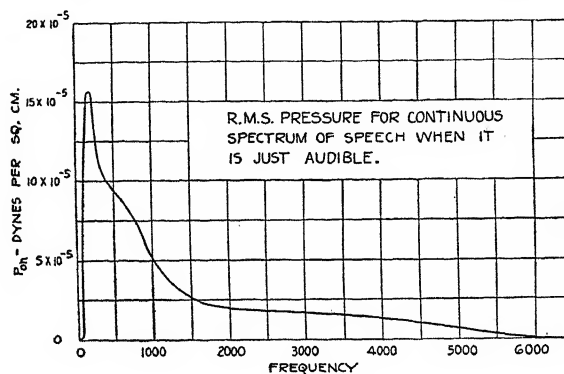


Fig. 6

70 in order that the loudness of the initial tone be equal to 83. The curves in Fig. 5 were calculated in this way for various high and low-pass filters and at various levels of the initial tone. The points were obtained by experiment.

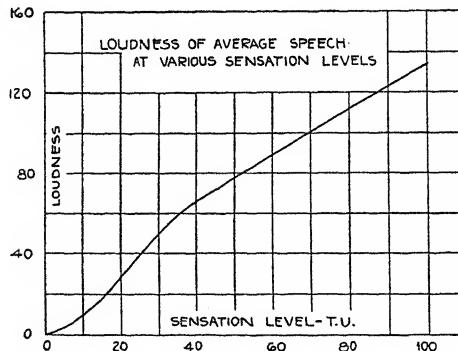


Fig. 7

Figs. 6 to 8 give similar results for average speech. The speech was picked up and transmitted to the ear by a system having approximately a uniform response so that the spectrum at the ear was essentially the same as that at the transmitter diaphragm. Neither of the formulas developed above are directly applicable to the calculation of the loudness of average speech. The summation method is applicable to the vowel

sounds when their spectra are known. It would, however, be too laborious to calculate the loudness of all the vowel sounds in order to obtain the loudness of average speech. It has been found convenient to treat average speech as a continuous flow of energy and use the formula for calculating the loudness of such spectra. The interval  $\Delta n$  was determined from the average fundamental of the male voice to be 128 cycles. The relative energy distribution of speech was obtained from the measurements that were made by Crandall and Mackenzie. The spectrum in Fig. 6 was

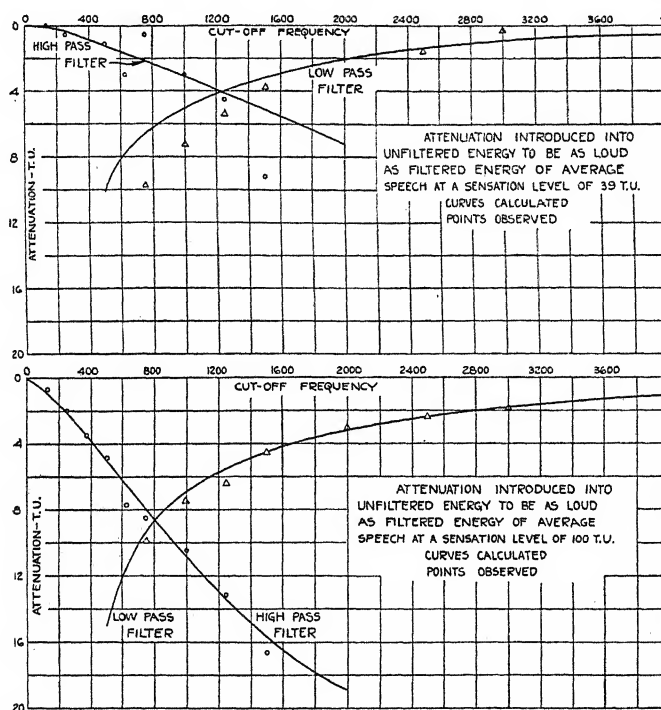


Fig. 8

obtained from the relative distribution by means of Eq. (11), where  $\Delta n$  has the above value and  $P_0$  is the minimum audible pressure for an 800-cycle tone. The loudness of speech is determined largely by the sustained portion of the vowel sounds so that although speech is represented as a continuous flow of energy it is necessary to take the interval as equal to the fundamental of a voice when we deal with loudness. The loudness of average speech calculated in this way agrees well with measured values of its loudness and also with the calculated loudness of sustained vowel sounds.



The calculated loss curves for both speech and test tone are pretty largely independent of the numerical values that are calculated for their loudnesses. They depend upon the changes in loudness as the sensation levels of the initial sounds are changed. The agreement between experimental and computed values gives an idea of the reliability of the equation. The observational error varies from  $\pm 1$  TU to about  $\pm 3$  TU, depending upon the quality differences of the sounds being compared. In any case, it is necessary to use seven or eight observers in order to get a reproducible average and in the case of speech, it is also necessary to use several callers. The equation agrees as well with similar data on other complex sounds, which are not shown here.

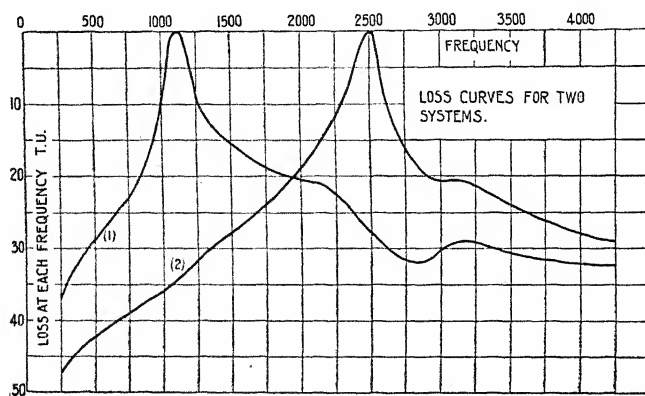


Fig. 9

Another case of interest is the loss caused by introducing known amounts of distortion into an otherwise distortionless system. As in the previous case, this loss was measured by attenuating the undistorted sound until it was as loud as the distorted sound. Results are given for the two types of distortion shown in Fig. 9, for the case of speech. These curves give the number of TU that the pressure at any frequency of undistorted speech had been decreased. Hence, the pressure spectrum for the distorted sound could be calculated from that shown in Fig. 6. The loudness of the distorted sound was then computed and the loss obtained graphically from Fig. 7. The curves shown in Fig. 10 were calculated in this way for various sensation levels of the initial speech.

#### DISCUSSION

In the case of single frequency tones, Eq. (17) reduces to the following form:

$$L_f = (10/3) \log_{10} S^{r/10} (W_f P_{0f})^{2r} . \quad (19)$$

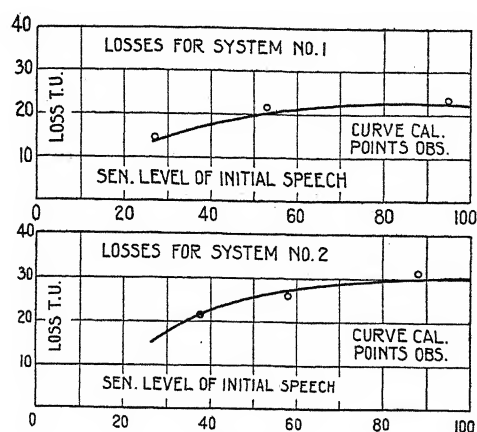


Fig. 10

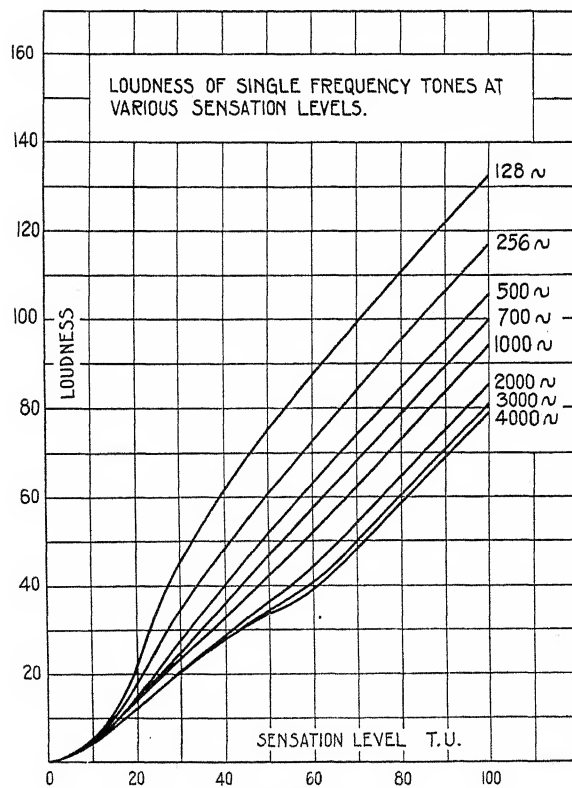


Fig. 11

Fig. 11 shows the loudness of several tones as calculated with the above equation. It will be seen that the calculated loudness is not in agreement with the commonly accepted idea that single frequency tones are equally loud when they are an equal number of TU above threshold. The equation predicts that the lower frequency tones increase in loudness much more rapidly than do the high frequency tones when their amplitudes are changed in equal ratios. Some preliminary experiments with single frequency tones have indicated that this is the case. Measurements are now under way for determining how the loudness of single frequency tones depends upon their sensation levels.

The reason that the calculated loudnesses of all tones do not increase at the same rate when their amplitudes are increased in equal ratios is due to the weight factors which are functions of both frequency and amplitude. It cannot be regarded as certain that the method of determining the weight factors from the data on complex sounds is unique. Hence, it is desirable to redetermine the weight factors directly from measurements on single frequency tones.

It will be recalled that the root factor  $r$  which is inversely proportional to the minimum perceptible increment of intensity ratio was taken as independent of frequency. Although it appears from the measurements of Knudsen that this is not strictly the case, it can be regarded as so without appreciable error. If  $r$  were to be made a function of frequency, the equation would be so complicated as to make it practically useless.

It appears that the loudness equation formulated here is consistent with the phenomena of one tone masking another.<sup>10</sup> The overall aspect of the masking phenomena is that a tone of given frequency masks a tone whose frequency is a given number of cycles above it much more than it does a tone the same number of cycles below it. This amounts to saying that by virtue of a 700-cycle tone being audible, the sensitivity of the ear to 1000 cycles is less relative to 400 cycles than it was when the 700-cycle tone was inaudible. Now it is natural to regard the weighting factor curves as indicative of the sensitivity of the ear from a loudness standpoint for different states of agitation of the ear. The state of agitation may be produced by either a single frequency or a complex tone. If we regard a 700-cycle tone as an agitating tone and change the state of agitation from 0 to 70 TU, the weight factor curves show that the sensitivity has been changed in the same direction as indicated by the masking experiments. It is to be noted, however, that the observed values of

<sup>10</sup> R. L. Wegel and C. E. Lane, *Phys. Rev.* **23**, 266 (Feb. 1924);  
H. Fletcher, *Jour. Frank. Inst.* **194**, 289 (Sept. 1923).

masking are the resultants of two effects, the change in ear sensitivity and the true sensation masking, that is, the inability to distinguish between sensations that are essentially the same.

BELL TELEPHONE LABORATORIES, INC.,  
NEW YORK CITY,  
July 17, 1925

## BOOK REVIEWS

**Light. (Second Edition).** H. M. REESE.—The first edition of this book appeared in 1921. This revised edition follows the same general plan. The chapter dealing with atomic theory has been changed and extended and thus brought more closely into touch with the latest advances in that field.

The letters on many of the diagrams are small and indistinct thus making it difficult to locate them. For the inexperienced student it is confusing to change the convention in respect to sign as one passes from refraction to lenses. In a book of this grade it would be desirable to include a brief discussion of thick lenses. Many would prefer to use the projection of uniform circular motion on a diameter as an *illustration* rather than as a *definition* of simple harmonic motion.

On the whole the book is admirably suited to the purpose for which it was written. The fundamental principles are presented in a clear and simple fashion without being encumbered by a mass of details. The treatment of diffraction and interference is especially good. As an introduction to more advanced and detailed study the student should find the book very attractive reading, and the teacher who is interested in a simple and direct presentation of the subject will find in it many helpful suggestions.—  
Pp. xi+297. Missouri Book Co., Columbia, Mo., 1924. R. C. GIBBS

**Alternating Currents and Transients.** F. M. COLEBROOK.—In the first part of the book the author develops what is usually termed the "complex algebra" or "symbolic" method of treating alternating current problems; in the second part the method is illustrated by practical applications. The author brings into harmony the nomenclature of pure vector analysis and of the rotating-vector method in alternating current theory. The author considers that the interpretation of the symbol  $j$  as the imaginary quantity  $\sqrt{-1}$  is neither necessary nor desirable and that the introduction of the terms "imaginary" or "complex" is a hindrance. The symbol  $j$  is initially defined as an operator that rotates a vector through  $90^\circ$  in a certain direction. On the basis of this simple definition, the author builds up the whole structure of the rotating vector method.—Pp. x+195. Price \$3.00. McGraw-Hill Book Company, 1925. FREDERICK BEDELL

## THE PHYSICAL REVIEW

### THE FINE STRUCTURE OF CERTAIN X-RAY ABSORPTION EDGES

BY KATHERINE CHAMBERLAIN

#### ABSTRACT

**X-ray absorption edges for certain elements and compounds.**—In a recent paper Coster<sup>1</sup> reports a white line on the long wave-length side of the x-ray absorption edge of some metallic oxides. Evidence is here reported which shows that in each case the white line is the absorption edge for some of the material which had been reduced to the metal by the x-ray beam. Screens were prepared by covering black paper with a thin layer of finely divided metal weighing 2 to 3 mg per cm<sup>2</sup>. (1) *K absorption edges for Ti(22), V(23), Cr(24) and Mn(25)* were found at 2489.5, 2261.9, 2064.9 and 1891.4 x-units. (2) *L<sub>III</sub> absorption edges for Sn(50), Sb(51) Te(52) and I(53)* are 3146.9, 2291.5, 2847.1 (Coster) and 2712 (Coster). These values are all in good agreement (within less than 1 x-unit) with the positions of Coster's white lines. (3) *In the case of compounds of higher valence*, the white line Coster obtained is therefore due to reduced element. (4) *In the case of sulfides and sulfitcs*, the secondary absorption edge at 4988 x-units reported by Lindh<sup>2</sup> may likewise be due to traces of sulfate in the screen produced by the action of the x-rays.

**Chemical changes produced by x-rays.**—Chemical evidence of appreciable reduction of iodic acid and of potassium permanganate is presented, and also of the oxidation of sulfurous acid.

**Theory of changes of valence produced by absorption of radiation by elements 22-25 and 50-53 and of consequent chemical changes.**—It is proposed that the numerous electron transitions that follow the removal of an electron from its normal orbit by absorption of radiation may occasionally occur in such a way as to result in a change in the general electron configuration such that some of the valence electrons find stable positions farther in, thus resulting in a reduction of valence. Oxidation can also occur when the change in the electron configuration is such as to place an increased number of electrons in the valence group. What makes this proposal seem especially reasonable is that Ti(22), V(23), Cr(24) and Mn(25) occur in a portion of the periodic table in which inner groups are being filled in building new elements while Sn(50), Sb(51), Te(52) and I(53) are found very close to such a group. Bohr thus considers that configurations which place additional electrons in inner groups in this region are stable.

**I**N a recent article<sup>1</sup> Coster describes the K absorption edges of titanium, vanadium, chromium and manganese and the L<sub>III</sub> absorption edges of tin, antimony, tellurium and iodine, obtained when various compounds

<sup>1</sup> Coster, Zeits. f. Phys. (July 2, 1924).

were used in the absorbing screens. He found a complicated structure of the absorption edge in each case for the more highly oxidized compounds used. An important feature of the structure was a white line on the long wave-length side of the absorption edge about six or seven x-units from the main edge. It is the purpose of this investigation to inquire further into the significance of this white line. It is not found when the free element or a compound of low valence is used in the absorbing screen.

Coster's data which have to do with the present investigation are given in Tables I and II.

TABLE I

*Coster's data for titanium to manganese.*

Element	Screen	K absorption edge	White line $K\alpha$	Valence
Titanium(22)	TiO <sub>2</sub>	2482.9x	2489.5x	4
	Ti metal	2484.0		
Vanadium(23)	V <sub>2</sub> O <sub>5</sub>	2256.4	2262.8	5
	V <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	2256.7		3
Chromium(24)	Na <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>	2059.5	2065.0	6
	K <sub>2</sub> CrO <sub>4</sub>	2059.1	2065.2	6
	Cr <sub>2</sub> O <sub>3</sub>	2060.6		3
	[Cr(NH <sub>3</sub> ) <sub>6</sub> ](NO <sub>3</sub> ) <sub>3</sub>	2063.8		3
	CrCl <sub>3</sub>	2063.0		3
Manganese(25)	KMnO <sub>4</sub>	1886.0	1891.3	7
	KMnO <sub>4</sub> (reduced)	1887.5		
	Mn <sub>2</sub> O <sub>4</sub>	1888.9		
	Manganic acetate	1887.8		3
	MnSO <sub>4</sub>	1889.2		2

TABLE II

*Coster's data for tin to iodine.*

Element	Screen	L absorption edge	White line $L_{\alpha\alpha'}$	Valence
Tin(50)	SnO <sub>2</sub>	3140.6x	3147.5x	4
Antimony(51)	KSbO <sub>3</sub>	2984.1	2990.8	5
	Sb <sub>2</sub> O <sub>3</sub>	2985.1	2991.1	3
Tellurium(52)	H <sub>2</sub> TeO <sub>4</sub>	2840.6	2846.6	6
	H <sub>2</sub> TeO <sub>3</sub>	2842.2	2846.9	4
	Te metal	2847.1		
Iodine(53)	HIO <sub>4</sub>	2705.8	2711.3	7
	HIO <sub>3</sub>	2707.1	2711.5	5
	KI	2712.2		1
	I	2712		

It will be noted that the wave-length of the absorption edge increases slightly as compounds of lower valence are used in the absorbing screen; also that the white line is, in general, found only with compounds repre-



sending the higher valences and never with the free elements. Moreover, the values for the absorption edges of the free element in the case of both iodine and tellurium fall within a fraction of an x-unit of the white line reported for the oxidized states. This at once suggests that the white line may be the absorption edge of a portion of the material in the absorbing screen that has undergone reduction and that the x-ray beam is the reducing agent.

#### EXPERIMENTAL DETAILS

The present work was undertaken to investigate the hypothesis that x-rays might reduce part of the highly oxidized compound in passing through the absorbing screen and that the white line reported by Coster might be the simple absorption edge of the reduced portion. The resulting investigation took a two-fold course. In the first place, certain of the compounds used by Coster were exposed to x-rays for a number of hours in the effort to discover whether reduction of the highly oxidized compounds could be demonstrated chemically. In the second place, spectrograms were made of the  $L_{III}$  absorption edges of metallic antimony and tin and of the K edges of metallic titanium, vanadium, chromium and manganese to discover whether these would coincide as closely with the white lines obtained with the corresponding oxidized compounds as do the edges for iodine and tellurium in Coster's data.

For the chemical part, the procedure was as follows. Portions of a 25 percent solution of iodic acid in water were introduced into thin walled specimen tubes. These were filled about three fourths full and the neck of the tube rinsed carefully with distilled water before sealing off, to prevent possible reduction of any of the iodic acid by the heat of the blast lamp. One of these tubes also contained about 1 cc of carbon tetrachloride, another, the same amount of chloroform, a third, the same amount of carbon disulphide while several other tubes contained only iodic acid and were broken open and tested with the organic solvents after x-raying. The tubes were placed in a lead covered box containing a Coolidge tube and were exposed to x-rays for about 14 hr with a tension of 35000 volts, a current of 30 milli-amp., and a distance from target to specimen tube of about 5 inches (13 cm). Every sample gave indications of traces of free iodine by imparting a distinct pink coloration to the organic solvent.

The iodic acid was carefully tested with chloroform and found entirely free from iodine before exposure to the x-rays, a precaution that is quite necessary as iodine or iodide in traces frequently contaminate iodic acid. The carbon disulphide was of only technical grade and so not

above suspicion in regard to purity but the chloroform and the carbon tetrachloride had been especially purified for analytical work. Blanks treated exactly as were the other samples except that they were not exposed to the x-rays gave negative tests for iodine. The conclusion is, therefore, that traces of the iodic acid were reduced by the x-rays.

A solution of potassium permanganate, another of the compounds reported by Coster, was next used. This solution was so dilute that the permanganate imparted only a faint pink color to the water. It was placed in a glass stoppered Erlenmeyer flask and exposed to x-rays for two hours. By the end of that time the pink color had entirely disappeared, thus showing undoubted reduction of the permanganate ion.

The remainder of the investigation consisted in getting the  $L_{III}$  absorption for antimony and tin and the K absorption for titanium, vanadium, chromium and manganese, using the free metal in each case to make the absorbing screen. All of the spectrograms were made with a Siegbahn spectrograph similar to that used by Coster. The source of high potential was a small transformer giving a maximum potential of 20,000 volts. The potential was controlled by a rheostat in the primary circuit. The rough pump was a General Electric oil pump which was connected both to the x-ray tube and to the spectrograph chamber. A Gaede molecular pump was used as a finishing pump to produce a sufficiently high vacuum in the x-ray tube. Tungsten filaments were used throughout except for titanium when a molybdenum filament was used to prevent possible overlapping of the edge by tungsten lines in the second order.

In most cases the absorbing screens were made by grinding the metals as finely as possible in an agate mortar and then rubbing on pieces of the black paper which is placed by the Eastman Company between pieces of cut film to protect the sensitive emulsion. New screens were made for the duplicate plates in every case where there was any chance that the metal on the screen might have become oxidized by exposure to the air or changed in any other way.

Tin offered special difficulties because its malleability made it impossible to grind it fine, at least at ordinary temperatures. Moreover while it is brittle above 200°C, it proved impossible to get it ground to the necessary degree of fineness at that temperature. The thinnest tin foil would make an absorbing screen many times as thick as was desired. The method finally used was to precipitate the tin from a slightly acid solution of stannous chloride by placing a sheet of zinc in it. The dark gray sludge thus deposited was scraped off and washed repeatedly with distilled water leaving the tin in flat particles having a metallic luster. The finer particles were separated by swirling in water until all the par-

ticles were in suspension, then allowing the heavier particles to settle out and removing the lighter particles by decantation. This was repeated several times. A Gooch crucible was next fitted with an alundum disk and a piece of the black paper, and a sufficient quantity of the suspension of tin particles in water was filtered through it to cover the black paper with a thin continuous layer of metallic tin. The paper and adhering tin were then dried over a Bunsen flame. In this way an absorbing screen was made which showed no uncovered portions and had a bright metallic luster. The total weight of tin was approximately 3 mg per cm<sup>2</sup>. The same method was followed in making one of the absorbing screens used for antimony. It would also have been possible with tellurium but not with chromium, vanadium, manganese or titanium, as these are not reduced to the free metal by zinc. These are, however, sufficiently brittle so that they can be ground to the necessary degree of fineness in an agate mortar and applied to the paper in the dry state.

The weight of absorbing metal was between 2 and 3 mg per cm<sup>2</sup> except one each of Mn and Ti which were 7.5 and 3.6 mg, respectively. In the case of iodine, iodic acid, pure or impure, was used.

Considerable variations in the amount of material on the absorbing screen apparently make little difference in the appearance of the edge. Thicker screens necessitate longer exposures which may have a tendency to obliterate detail by covering it with an excessive amount of secondary radiation. Thin screens are therefore preferable. It would also appear necessary to use samples of the metals that are as pure as possible. The first sample of metallic chromium used was not highly purified and contained a certain amount of slag. Absorbing screens made from this gave spectrograms showing an absorption edge that differed from Coster's white line by several x-units. When a purer sample of metallic chromium was obtained, however, the check was entirely satisfactory.

In certain cases, special precautions had to be taken because the absorption edge was obscured by an emission line. The L<sub>III</sub> edge of tin falls very close to the L $\alpha$  lines of iodine. In spite of the fact that several plates had been made since any iodine compound had been placed in the tube, these lines both appeared, making the location of the edge somewhat uncertain. It was therefore necessary to scour the interior of the x-ray tube and the target with alundum polishing powder until all discoloration of the brass interior of the tube had been removed. A new focussing cylinder was also put around the filament. After this plates were secured that showed no sign of iodine lines. The titanium edge lies within a few x-units of the L $\beta_2$  line of tungsten in the second order. The tube was

therefore cleaned again and a molybdenum filament used instead of tungsten.

It happened that suitable reference lines fell at convenient places on most plates because of the characteristic radiation of the metals in the x-ray tube. Chromium, manganese, vanadium or titanium salts were not used to obtain reference lines as the  $K\beta_2$  lines fall very close to the K absorption edges and there appeared to be danger that faint traces of these lines, if present, might be mistaken for the absorption edges. The only exception was in the case of manganese. Potassium permanganate solution was put on the target and reduced to manganese dioxide by evaporation to dryness in order to use the  $K\alpha_1$  line of manganese as a reference line to determine the chromium edge. It was not done, however, until after the manganese absorption had been completed so that there was no danger of obscuring the manganese edge from this source.

Table III gives the values for the white lines reported by Coster on the long wave-length side of the absorption edge for the compounds of higher valence and the simple absorption edges obtained by the writer for the free elements<sup>2</sup> and by Coster for tellurium and iodine.

TABLE III  
*Absorption edges of free elements.*

Element	Screen	White line (Coster)	Absorption edge of free element	Difference Line—edge
Ti	TiO <sub>2</sub>	2489.5x	2489.5x	0.0
			2484.0(Coster)	(5.5)
V	V <sub>2</sub> O <sub>5</sub>	2262.8	2261.9	0.9
Cr	Na <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>	2065.0	2064.9	0.1
Cr	K <sub>2</sub> CrO <sub>4</sub>	2065.2	2064.9	0.3
Sn	SnO <sub>2</sub>	3147.5	3146.9	0.6
Sb	KSbO <sub>3</sub>	2990.8	2991.5	-0.7
Sb	Sb <sub>2</sub> O <sub>3</sub>	2991.1	2991.5	-0.4
Mn	KMnO <sub>4</sub>	1891.3	1891.4	-0.1
Te	H <sub>2</sub> TeO <sub>4</sub>	2846.6	2847.1 (Coster)	-0.5
Te	H <sub>2</sub> TeO <sub>3</sub>	2846.9	2847.1 (Coster)	-0.2
I	HIO <sub>4</sub>	2711.3	2712 (Coster)	-0.7
I	HIO <sub>3</sub>	2711.5	2712 (Coster)	-0.5

In every case, with the exception of Coster's value for titanium, the absorption edge of the free element coincides within the limits of experimental error with the white line. Apparently, Coster's sample of titanium had become oxidized for Lindh reports a value for the titanium edge in

<sup>2</sup> The data for tellurium, iodine, antimony, and tin were reported together with the hypothesis proposed here, in *Nature*, October 4, 1924. Confirmatory data upon titanium, vanadium, chromium and manganese have appeared in an article by Lindh (*Zeits. f. Phys.*, February 11, 1925). His value for the absorption edge of metallic titanium is 2491.2 x-units.

substantial agreement with that of the present writer.<sup>2</sup> It would therefore seem conclusive that the spectrographic data for all eight elements concerned corroborate the chemical evidence of reduction obtained with iodic acid and potassium permanganate. One more piece of evidence in regard to the origin of the white lines can be offered here. Plates were made of the absorption with iodic acid using in one case a sample of the acid known to be free from the reduced forms of iodine and in the other, a sample that gave a test for contamination with traces of iodide or iodine. Both plates showed the white line but it was clearer on the plate made with the impure acid.

The evidence obtained would indicate that only traces of the material in the absorbing screen are reduced. Thus, we should expect the effect upon the photographic plate to be similar to that produced by a very thin absorbing screen. With such screens practically all the absorption is frequently confined to a very narrow band which gives the appearance of a white line on the plate such as Coster describes.

Certain evidence has been obtained that the x-ray beam can oxidize quadrivalent sulfur in sulfurous acid to the hexavalent form which would indicate that this is at least a contributing cause in the production of the secondary edges which Lindh reports in the neighborhood of 4988 x-units for the lower valence forms of sulfur.

The general plan was to make an acid solution of a soluble sulfite containing a small amount of barium chloride which, in the presence of sulfate, will precipitate barium sulfate, a very insoluble, dense, crystalline precipitate. It proved impossible to secure any sample of sodium sulfite prepared by the manufacturers of chemicals that was not contaminated with considerable quantities of sulfate. This is probably characteristic of all sulfites, and to a considerable extent of sulfides, that they will not be free from traces of sulfate unless special precautions are taken to prepare them in an atmosphere free from oxygen and to keep them from the oxygen of the air during use.

It was therefore decided to prepare a solution of sulfurous acid in water containing a small amount of barium chloride by saturating it with sulphur dioxide and to expose the solution thus formed to the x-ray beam to discover whether any of it would become oxidized to sulphate. The preparation of sulfurous acid free from all traces of sulfate proved rather difficult. The sulfur dioxide procurable in tanks contained sufficient oxygen to oxidize an appreciable amount of the sulphurous acid. The procedure finally adopted was as follows. Bulbs having a capacity of about 50 cc and a very thin wall were blown on one end of glass specimen tubes and the tubes were constricted above the bulb to facili-



tate sealing off after the specimen had been prepared. The whole was fitted with a two hole stopper, a delivery tube leading to the bottom of the bulb, and an outlet tube. Meanwhile, a sulfur dioxide generator had been set up containing about two hundred grams of acid sodium sulfite and about four hundred cubic centimeters of water. Concentrated sulfuric acid could be admitted as required through a dropping funnel. The generator was connected to a water trap, to insure that no sulfuric acid should be carried over, and then to the bulb. Before use, the generator was allowed to operate for some time to be certain that all air was removed. Meanwhile, one of the bulbs was filled with conductivity water, the purest distilled water obtainable, and boiled under a reflux condenser for about fifteen minutes to remove any oxygen that might be dissolved in the water. It was then connected as quickly as possible to the sulfur dioxide generator and sulfur dioxide passed in for about an hour and a half. By the end of this time, the contents of the bulb had cooled to room temperature and were saturated with the gas so the bulb was immediately sealed off in the flame of a blast lamp.

In this way two samples were prepared entirely free from turbidity. They were set aside for about ten hours as a precipitate is sometimes very slow in forming. When no precipitate had formed by the end of this time, however, it seemed conclusive that neither sulfate nor oxidizing agent capable of producing any was present in either bulb.

One was therefore set aside as a blank and the other exposed to the x-ray for about forty milli-ampere hours under a tension of a hundred and ten thousand volts. By the end of this time a small amount of barium sulfate had been precipitated thus demonstrating that traces of the material had become oxidized by the x-ray beam for the bulb that had not been x-rayed remained clear. Later, in order to make the test more conclusive, the other specimen was also exposed to the x-ray beam and a precipitate formed.

Lindh<sup>3</sup> has questioned the real existence of a secondary absorption edge in the case of quadrivalent sulfur because of the readiness with which it undergoes oxidation. The present writer would go a step farther and question whether any of the secondary edges reported by him at a wavelength in the neighborhood of 4988 x-units for divalent and quadrivalent compounds of sulfur are other than the simple absorption edges of hexavalent sulfur. Our experience here would indicate that the principal oxidizing agent is probably the oxygen of the air but the x-ray beam itself is quite evidently a contributing cause.

<sup>3</sup> Siegbahn, *Spektroskopie der Röntgenstrahlen*, p. 142.

## UNDERLYING THEORY OF THIS ABSORPTION

It will next be of interest to consider the bearing of these results upon the Bohr theory. While nothing definite has been said by Bohr regarding the valence electrons of these elements, the inference has always been that these are located in the electron groups of highest quantum number, i.e. in those groups representing electron orbits having the greatest major axes. Lewis,<sup>4</sup> Bury,<sup>5</sup> and J. J. Thomson<sup>6</sup> carry this a step farther and suggest that oxidation and reduction changes represent an increase or decrease in the number of electrons in the valence ring by a change in the number of electrons in inner groups. These outer electrons are the electrons that give rise to optical spectra, and require so little energy to eject them from their normal orbits to the periphery of the atom or beyond, that radiation of longer wave-length than that considered here will be required. Therefore, the way in which they are most likely to be removed by x-radiation is by what we may call the indirect method.

The mechanism of the process may be somewhat as follows. Below is the electron arrangement given by Bohr for titanium.

Group	K	L	M	N
Quantum numbers	1 <sub>1</sub>	2 <sub>1,2</sub>	3 <sub>1,3,3</sub>	4 <sub>1</sub>
Number of electrons	2	4,4	4,4,2	(2)

Since the atomic number of titanium is 22, only four groups of orbits, K, L, M and N, are possible. The energy level diagram shows one K level, three L levels, five M levels and one N level.

Suppose that radiation of the frequency required to eject an electron from the K orbit outside the atom is allowed to fall upon a titanium absorbing screen. The possible transitions, taking proper account of the Selection Principle, by means of which the vacant place may be filled again, are as follows. An electron might fall from the M<sub>3</sub> level to the K giving rise to radiation of the frequency designated as the K $\beta_1$  line. The vacant place in the M<sub>3</sub> level might then be filled by an electron from the N level and the electron originally ejected from the K to the periphery might fall back into the vacant place in the N. This is a typical case only, for a variety of transitions are possible, but the point is that any such phenomenon involves numerous transitions between the various electron orbits. It would therefore seem possible that, as a result of all these transitions, in certain cases a sufficient alteration of the atomic configuration might occur so that the possible number of electrons in groups of lower quantum number might increase, thus providing for more

<sup>4</sup> Lewis, Jour. Am. Chem. Soc. 38, 770 (1916).

<sup>5</sup> Bury, Jour. Am. Chem. Soc. 43, 1602 (1921).

<sup>6</sup> J. J. Thomson, The Electron in Chemistry, p. 96-99 (1923).



electrons in such groups and a corresponding reduction in the number of electrons in the valence group. This would seem to be a reasonable extension of Bohr's hypothesis regarding the formation of the rare earth group.

It will be recalled that he accounts for the formation of this group by the hypothesis that when electrons are added to compensate for the increased nuclear charge in passing from element to element, they are inserted into groups of lower quantum number. Thus, the most stable position open to the last added electron is at times in an electron group of lower quantum number than that available for those added just previously. In other words, at certain points in the up-building of the elements, electrons begin to be inserted again into groups of lower quantum number that had previously been in a state of temporary completion. If this occurs in the building up of new elements, it seems reasonable to inquire whether it might not occur also in a particular element when x-radiation falls upon it and produces numerous electron transitions in its atoms. Some of these transitions may produce a change in the configuration of certain orbits that would provide stable positions for part of the valence electrons in orbits of lower quantum number, thus resulting in a reduction of valence. Moreover, if some of the valence electrons were moved to positions in groups of lower quantum number, they would exert a shielding effect upon the outer electrons with a consequent slight reduction in the energy of these outer orbits. As a result, it would be expected that the different absorption edges would represent slightly less energy when the element exists in its lower valence forms; i.e., the wave-length of the edge would be slightly longer for a compound of low valence than for one of high. It will be noted that this is exactly what is found when the absorption edges are determined experimentally for the different valence forms of the same element.

If the mechanism of the process is as proposed here, oxidation as well as reduction by the x-ray beam may be considered possible. In fact, even if these changes of electron configuration occur only temporarily, they may be expected to produce an effect upon the absorption edge. Oxidation effects produced in this way would probably not be visible in many cases for the edge of the oxidized form would fall on the short wave-length side of the main edge; i.e. in that region in which absorption is already at a maximum, so that it would not be likely to be visible except in the case of those elements whose absorption edges for the various valence forms differ from each other by a number of x-units. Sulfur is an element whose absorption edges meet this requirement and

Lindh's data<sup>7</sup> showing multiple edges in the case of certain of its compounds exhibit rather greater agreement in wave-length between the secondary edges of lower valence compounds and the principal edges of those of higher valence than seems reasonable to attribute to chance. At least it seems reasonable to consider that the first secondary edge reported by Lindh<sup>3</sup> for various sulfides and sulfites is due to the presence of traces of hexavalent sulfur in the absorbing screens, as compounds of these kinds are slowly oxidized by exposure to the oxygen of the air. Moreover, sulfides and sulfites that are entirely free from traces of sulfate are almost unknown. It has also been shown that the x-ray beam itself can bring about oxidation of a portion of the material in the absorbing screen.

Attention might be called to the fact that titanium, vanadium, chromium, and manganese occur in a region in the periodic system in which Bohr proposes that the added electrons in building new elements are being inserted into inner groups. While it is true that the tin, antimony, tellurium, iodine group is built up by inserting electrons in the groups of highest quantum number rather than in inner positions, it seems significant to note that they come only three elements below the rare earth group and here, again, electrons begin to be inserted into inner groups. Thus, we find that both of these groups of elements that are capable of oxidation and reduction either fall in a portion of the periodic table in which electrons are being inserted into inner quantum groups or very close to such a portion. This would seem to make it extremely probable that electron shifts from outer to inner groups or vice versa may take place here in a particular element and that these shifts would result in a change of valence.

Exactly to what extent valence changes in the absorbing screen can account for the fine structure of absorption edges, it will be impossible to say until more data are available. Evidently, however, such changes must be taken into account in the interpretation of all absorption edges involving elements that are capable of oxidation and reduction and they may explain much that has previously been obscure regarding fine structure. Moreover, it may prove possible to reverse the process and interpret chemical valence in the light of the Bohr theory by a study of the absorption edges of elements that are capable of oxidation and reduction. Last, a systematic study of x-rays as an oxidizing or reducing agent for inorganic compounds may give the key to the solution of that vastly more difficult problem of what occurs in the human body when x-rays are used as a therapeutic agent.

<sup>7</sup> Lindh, Dissertation, Lund (1923).

In conclusion, I should like to express my thanks to Dr. George A. Lindsay, of the University of Michigan, for the use of a Siegbahn spectrograph and for valuable criticism during the progress of this work, to Mr. William Fink and Mr. James Kassner for helpful suggestions in regard to the chemical part of this investigation, and to Dr. Coster for his interest in my preliminary report and for the encouragement he offered to carry the work farther.

PHYSICS LABORATORY,  
UNIVERSITY OF MICHIGAN,  
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CHARACTERISTICS AND SPECTRA OF LOW VOLTAGE ARCS  
IN  $H_2$ ,  $N_2$  AND IN MIXTURES OF  $H_2$  WITH Hg AND  $N_2$ 

By C. T. KWEI

## ABSTRACT

I. *Arc characteristics.*—The tube used was a spherical bulb containing a Ni disk electrode and a W spiral filament and provided with a quartz window and an appendix in which could be placed liquid Hg. By applying corrections for filament drop and for initial velocities, approximately measured by use of a high resistance voltmeter, remarkably consistent values for the breaking voltages were obtained. (1) *With pure hydrogen*, there were no oscillations; the arc broke at the *ionization potential* 16.2 volts; and by plotting the  $2/3$  power of the current as a function of the voltage, the ionization potential of the atom was located at 13.7 volts. These voltages are subject to a correction of about  $-0.5$  volt for contact potential difference. (2) *With pure nitrogen*, the breaking potential 16.2 is not the ionization potential since oscillations occur below 16.9, the actual ionization potential, as shown by oscillograph observations. (3) *In mixtures of  $H_2$  with Hg*, a careful study was made for pressures of  $H_2$  from 0.1 to 3.0 mm, and with the Hg appendix at room temperature and at  $100^\circ C$ . Below a critical pressure of  $H_2$ , depending on the Hg pressure, oscillations of one or two types occurred. With the filament not too hot, 0.8 mm of  $H_2$  and Hg at  $20^\circ C$ , two arcing and two breaking potentials were observed. The curve as far as the second arcing potential, was reversible. The difference between the two arcing potentials is about 10.4 volts, the ionization potential of Hg. When a single breaking potential was observed, it decreased with the pressure of  $H_2$ , being approximately a weighted mean of the breaking potentials in the pure gases. (4) *Mixtures of  $H_2$  and  $N_2$*  behaved similarly to the mixtures with Hg. The breaking potential reached a minimum value for equal pressures of  $H_2$  and  $N_2$ . Under some circumstances two arcing potentials (3 volts apart) and two breaking potentials were observed. Oscillations of two types were likewise obtained. A break was observed at 22.7 volts which seems to be a critical potential for  $N_2$ .

II. *Spectroscopic observations.*—(1) *In  $H_2$* , the Balmer lines and secondary spectrum appeared together. (2) *In mixtures of  $H_2$  with Hg*, the Hg lines ( $2p-ms$ ) and ( $2p-md$ ) were weak below the second arcing potential and much intensified above it, while the secondary  $H_2$  spectrum and other bands were weakened or disappeared. (3) *In mixtures of  $H_2$  with  $N_2$* , evidence was obtained which indicates that the *ultraviolet band of ammonia*, associated with the 22.5 volt critical potential, is due to a molecule  $NH_x$ , where  $x$  is probably 3, and that the *Schuster band* is emitted only in the presence of oxygen and is due to a molecule  $N_xH_yO_z$ , possibly  $NH_4OH$ . This band was observed only at voltages higher than the critical voltage for "active nitrogen," 70.

## INTRODUCTION

RECENT experiments in low-voltage arcs have yielded a number of interesting, though in some cases puzzling, results. It is now known that arcs may be maintained in gases and vapors at voltages as low as

their ionizing potentials and in certain monatomic gases as low as their radiating potentials. The latter phenomenon is generally accounted for by the theory<sup>1</sup> that cumulative action is largely responsible for the ionization of partially ionized or excited atoms. Cases were also observed in which arcs were maintained at voltages too far below the radiating potentials to be accounted for by the velocity distribution of electrons. These were found to be due to oscillations in the arc such that the maximum voltage peaks would always be higher than the radiating potentials. This fact was independently discovered by Bär, v. Laue, and Meyer<sup>2</sup> and Eckart and Compton.<sup>3</sup> The last mentioned authors<sup>4</sup> were also able to maintain abnormal low voltage arcs in argon, helium and mercury vapor without oscillations and demonstrated by means of an exploring electrode that the cathode drop was invariably near the radiating potential and that the abnormal low voltage was due to a reverse field between the cathode drop and the anode, which they attribute to the diffusion of electrons, maintained by concentration gradient, against an electric field.

Duffendack<sup>5</sup> studied the low voltage arcs and the associated spectra in several diatomic gases—hydrogen, nitrogen, and iodine. He was able to determine the ionization potential for atomic hydrogen by maintaining an arc in the gas dissociated by means of an electrically heated tungsten tube furnace, and the value thus determined was in good agreement with Bohr's predictions. Similar results were obtained in iodine. In nitrogen, the dissociation was not appreciable when the arc struck, but above 70 volts the conductivity of the arc rapidly increased, and a brilliant flare appeared which Duffendack identified with the formation of "active nitrogen" as described by Strutt.<sup>6</sup> More recently Richardson and Tanaka<sup>7</sup> studied the striking and breaking potentials in hydrogen and concluded, as did Duffendack, that the breaking potential was a critical potential for the gas, but they differed from him in attributing it, from spectroscopic considerations, to the ionization of the hydrogen molecule as against dissociation plus ionization of one of the atoms. A recent important experiment by Smyth,<sup>8</sup> in which the positive ray method was employed in analyzing the ions formed in the hydrogen discharge,

<sup>1</sup> K. T. Compton, *Phys. Rev.* **20**, 283 (1922); Van der Bijl, *ibid.* **10**, 645 (1917).

<sup>2</sup> Bär, v. Laue and Meyer, *Zeits. f. Phys.* **20**, 82 (1923).

<sup>3</sup> Eckart and Compton, *Phys. Rev.* **24**, 97 (1924).

<sup>4</sup> Eckart and Compton, *Phys. Rev.* **25**, 139 (1925).

<sup>5</sup> Duffendack, *Phys. Rev.* **20**, 665 (1922).

<sup>6</sup> Strutt, *Roy. Soc. Proc.* **85A**, 219 (1911) et seq.

<sup>7</sup> Richardson and Tanaka, *Roy. Soc. Proc.* **106A**, 640 (1924).

<sup>8</sup> Smyth, *Roy. Soc. Proc.* **105A**, 116 (1924); *Phys. Rev.* **25**, 452 (1925).

seems to have decided definitely in favor of the ionization of the hydrogen molecule.

The work on low voltage arcs has now been extended to mixtures of gases and has already proven itself a promising method for investigating certain chemical properties of elements, such as combination and dissociation. In particular, although the synthesis of ammonia from hydrogen and nitrogen by electrical excitation was discovered over fifty years ago,<sup>9</sup> only a beginning toward analyzing the process has been made through the work of Andersen<sup>10</sup> and of Storch and Olson.<sup>11</sup> These authors detected the formation of ammonia in low voltage arcs in mixtures of hydrogen and nitrogen and by noting the rate of reaction concluded that the formation of ammonia in any appreciable amount occurred only after the arc was struck. Thus the critical potentials of the constituent gases and the rates of reaction as well as the spectra observed at various voltages afford several co-ordinating lines of approach towards a clearer understanding of chemical reaction.

To attack a slightly different problem, Duffendack and Compton<sup>12</sup> studied low voltage arcs in mixtures of hydrogen and mercury vapor and found that the dissociation of the hydrogen molecules in mercury arcs increased ten times in the 5 volt arc and three times in the 10 volt arc as a result of the presence of the mercury. This increase was explained as being due to "collisions of the second kind," in which the hydrogen molecules received the requisite energy of dissociation from excited mercury atoms in the  $2p$  states. In mixtures of nitrogen and mercury vapor, the dissociation (or perhaps activation) was found to be only one tenth as large.

Aside from the possibilities of studying combination and dissociation, the low voltage arc offers a convenient method for exciting spectra, for it removes certain objections usually connected with the flame or high voltage excitation. Thus the flame is incapable of excluding impurities present in it and may not furnish enough energy for excitation, and the high voltage discharge is likely to cause dissociation and release of occluded gases from the electrodes and walls. The purpose of our experiment then is to correlate the arcing characteristics in mixtures of gases with the spectra observable at various potentials.

<sup>9</sup> W. F. Donkin, Roy. Soc. Proc. 21, 281 (1873).

<sup>10</sup> Andersen, Zeits. f. Physik, 10, 64 (1922).

<sup>11</sup> Storch and Olson, Jour. Am. Chem. Soc. 45, 1605 (1923).

<sup>12</sup> Duffendack and Compton, Phys. Rev. 23, 583 (1924).



## APPARATUS AND METHOD

The apparatus consisted of a simple two-electrode discharge tube in the form of a spherical bulb 9 cm in diameter. The anode was a round nickel plate about 3 cm in diameter. The cathode was a hot filament made of 15 mil (.38 mm) tungsten wire wound closely in the middle into a helical spring of three turns. The electrodes were welded to tungsten leads which were sealed into ground glass stoppers and these in turn were sealed to the experimental tube by means of hard DeKhotinsky cement which was disposed so as to reduce to a minimum the presence of cement vapor in the tube. Vertically attached to the bottom of the bulb was a small glass appendix. When a mixture of mercury vapor and another gas was desired, this was filled 4 or 5 mm deep with mercury and could be heated up to the boiling point of water by immersing the tube in a water bath.

For spectroscopic observations, a side tube 15 cm in length and 1.7 cm in diameter was horizontally attached to one side of the bulb and a quartz window was fastened to it at the end. The light from any region between the target and filament or behind the filament was brought to a focus on the spectrometer slit by means of a quartz lens. The spectrum was observed with a direct reading constant deviation spectrometer for the visible region and photographs were taken with a small Hilger quartz spectrograph for the ultraviolet region.

The filament was heated through an adjustable carbon resistance by means of storage batteries. The voltage impressed on the plate was tapped from a potentiometer arrangement which was connected at will, by means of a double-pole double-throw reversing switch, to either the positive or negative side of the filament. It was found that the mean value of a critical potential from readings at the two positions was not always equal to the voltmeter reading plus or minus one half the filament drop of potential. In this experiment, only the mean values were taken.

The hydrogen and oxygen used in this experiment were prepared by electrolysis of dilute sulfuric acid. The nitrogen was prepared by dropping liquid bromine into concentrated ammonia, and was then made to pass through a wash bottle containing dilute ammonia and a second wash bottle containing dilute sulfuric acid to remove traces of bromine and ammonia, respectively. Each of these gases was stored in a drying tube for at least 24 hours over phosphorus pentoxide before it was admitted through a stop cock and a mercury cut off into a large reservoir 120 cm high and about 30 cm<sup>2</sup> in cross section. The large volume of the reservoir proved to be very convenient for adjustments at low pressures and re-



duced the rate of pressure change due to "clean-up." Another mercury cut off was inserted between the reservoir and two liquid air traps connected in series leading to the experimental bulb so that a small change in the pressure of the gas would be sensitively noticed by cutting off the large volume. The system was evacuated by means of a mercury diffusion pump backed by a high vacuum oil pump. For the identification of the ultraviolet and Schuster bands of ammonia, this gas was generated by evaporating a strong ammonia solution and the gas was dried by storing it over potassium hydroxide sticks.

Before a new gas was tried, the experimental bulb was usually baked for three or four hours in an electric furnace at a temperature between 300° and 350°C. The traps were constantly immersed in liquid air to condense any moisture or mercury vapor in the system, except when ammonia was used.

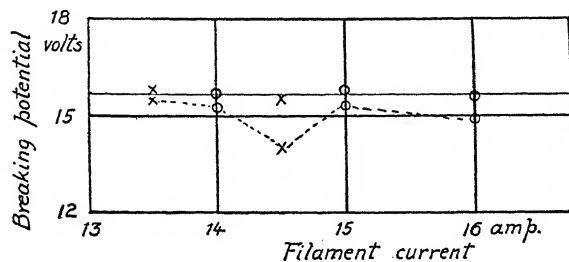


Fig. 1. Breaking potential in a mixture of  $N_2$  and  $H_2$ . Pressure for crosses was 0.8 mm, for circles 0.5 mm. The lower curve is uncorrected for "initial voltmeter" reading.

In agreement with Richardson and Tanaka<sup>7</sup> the writer found that when the filament current remained constant, the breaking potential of the arcs tended toward a minimum at a definite pressure. The minimum voltage was found at a pressure of about 0.5 mm, and the breaking voltages did not exceed this minimum by more than 0.25 volt between pressures 0.2 and 1.0 mm. The excess voltage at low pressures must be due to an insufficient supply of molecules to be ionized and at high pressures to energy losses which do not contribute to ionization. It was also found that with the increase of filament temperature, the breaking potential tended to diminish, probably due to the increase in initial velocities of the electrons. To correct this effect to a first approximation, a Cambridge and Paul universal test set was used as a high resistance voltmeter to measure the potential difference of the electrodes, acquired as a result of the thermionic emission only, before the impressed voltage was applied. When this reading, designated as the "initial voltmeter reading" was added, the various breaking potentials became much more uniform. Fig. 1 illustrates this point. This correction was made for all determina-

tions except those of a second arcing potential, where the variation of the second jump exceeded the value of the correction.

Since some of the apparent current-voltage characteristics were due to oscillations in the arc, these were detected and studied by use of a Western Electric cathode ray oscillograph, which was used so as to measure current and voltage along mutually perpendicular axes on the fluorescent screen.

#### ARC CHARACTERISTICS IN HYDROGEN AND IN MIXTURES OF MERCURY VAPOR AND HYDROGEN

Before the mixtures were tried, preliminary runs were made with hydrogen. The voltage-current characteristics were found to be very

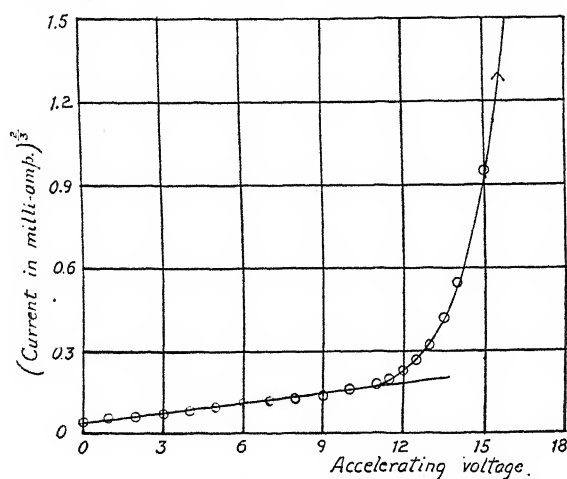


Fig. 2. Ionization potential of atomic hydrogen. Value observed 11.0 volts; with connections reversed 15.0 volts; mean value 13.0 volts. Initial voltmeter reading 0.5 volt. Corrected value 13.5 volts.

similar to those observed by Duffendack: 1. The potential of the break was always lower than the striking potential, usually by several volts, the difference being greater at higher pressures. In each case the varying factor was the striking potential while the breaking potential remained practically constant at 16 volts. 2. The breaking potential, pressure remaining the same, became slightly less with increasing filament temperature. This effect was corrected for by taking the "initial voltmeter" reading as described in the preceding section.

Limiting the pressure range to 0.4 to 1.0 mm, the corrected breaking potential as an average of sixteen runs was found to be  $16.17 \pm .05$  volts. An independent series of eleven runs was made several months later with different electrodes and the average was found to be  $16.23 \pm .03$  volts.

Both of these results are in excellent agreement with Duffendack's value of  $16.18 \pm .05$  volts. We shall take 16.2 as our experimental value for the ionization potential of the hydrogen molecule.

It was suspected that thermal dissociation due to the filament might furnish enough atoms to make the effect of atomic ionization detectable. Graphs were plotted on a magnified scale to see if the increase of current with voltage deviated from the  $i \propto V^{3/2}$  relationship. The point of departure of the curve from a straight line was taken as the value for the ionization potential for the hydrogen atom. Six graphs similar to Fig. 2 were plotted and the average potential came out to be  $13.67 \pm .14$  volts, which is near the 13.5 volt value calculated from the limit of the Lyman series.

When mercury was introduced into the appended tube, as described in the preceding section, and immersed in a water bath at room temperature, it was found that the *breaking potential* was systematically reduced in proportion as the relative amount of hydrogen in the presence of mercury vapor was diminished. The first two columns of Table I contain the experimental data.

TABLE I

*Arc in mixture of hydrogen with Hg vapor at room temperature*

Pressure of hydrogen	Breaking potential	
	(observed)	(calculated)
1.1 mm	16.34 volts	15.8 volts
.7	15.90	15.6
.35	15.22	15.1
.25	14.61	14.7
.15	14.27	14.2
.09	13.30	13.5

When the filament temperature was not too high, it was possible, in the mixture of hydrogen and mercury vapor maintained at room temperature, to locate a second striking potential when the pressure of hydrogen was at or below 1 mm. This is shown in Fig. 3. Very often when the voltage was lowered there were two breaking potentials, the first one being a volt or so lower than the second. Table II contains a summary of the readings.

It is seen that the two arcing and breaking potentials were observable at higher hydrogen concentrations. When the curve was retraced before the second arcing potential was reached, there was a marked approach to reversibility which is a prominent attribute of arcs with oscillations, as will be shown below. This is shown in Fig. 4. The breaking point here corresponds to the one observed in pure hydrogen.

*Interpretation of current-voltage relations in mercury-hydrogen mixtures.*  
It is rather surprising that two distinct breaks were not observed corresponding to the ionization potential for the hydrogen molecule at 16.2

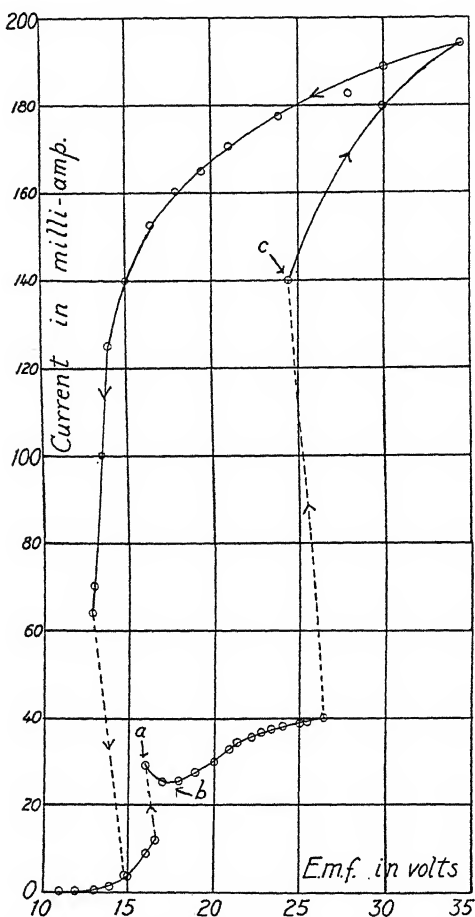


Fig. 3. Showing two striking potentials. Mercury appendix kept at room temperature. Pressure of hydrogen 0.75 mm. Readings uncorrected for filament drop.

TABLE II

*Arc in mixture of hydrogen and mercury vapor, with mercury appendix at room temperature*

Pressure of hydrogen	Striking potential		Breaking potential	
	1st	2nd	1st	2nd
mm	volts	volts	volts	volts
0.9	19.5	28.6	15.3	16.9
0.8	18.9	28.2	15.0	16.1
0.7		25.5		15.1
0.5		19.1		15.3
0.35		19.7		15.2

volts and for the mercury atom at 10.4 volts. An examination of the data suggests that the potential observed may be a weighted mean of the two critical potentials, depending upon the relative effectiveness of each constituent in neutralizing space charge around the filament. This

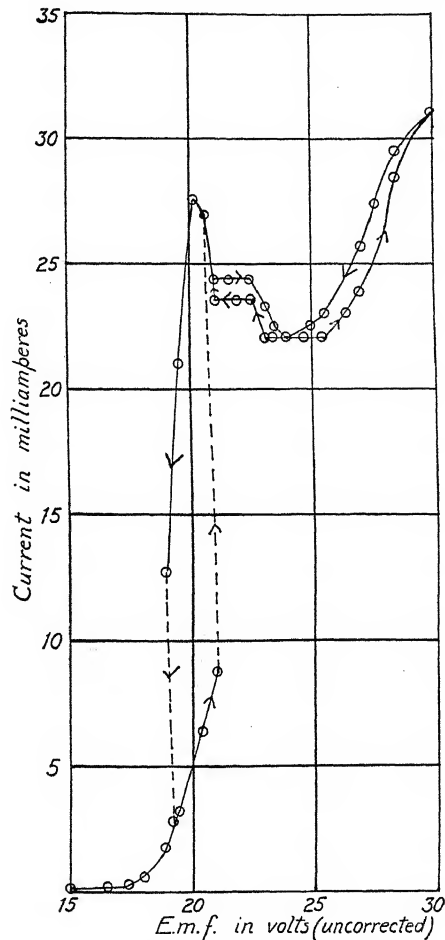


Fig. 4. Arc characteristics in mixture of mercury and hydrogen, when process was reversed before reaching the second striking potential.

depends upon the number of molecules of each gas present to be ionized, as well as the effective duration of the respective types of positive ions in the region of the space charge around the cathode.<sup>13</sup>

Let  $N_1$ ,  $N_2$  be the concentrations of mercury atoms and hydrogen molecules, respectively;  $T_1$ ,  $T_2$  be the average durations of the respective

<sup>13</sup> For theory of the low voltage arc consult K. T. Compton, *Phys. Rev.* 20, 183 (1922).

ions;  $V_1$ ,  $V_2$  their respective ionizing potentials. Then the weighted mean breaking voltages may be taken as

$$V' = \frac{N_1 T_1 V_1 + N_2 T_2 V_2}{N_1 T_1 + N_2 T_2} = \frac{T_1 V_1 + (N_2/N_1) T_2 V_2}{T_1 + (N_2/N_1) T_2}. \quad (1)$$

Now in an electric field of given potential drop, the hydrogen and the mercury ions will move in such a way that

$$\frac{1}{2} M_1 v_1^2 = \frac{1}{2} M_2 v_2^2, \quad (2)$$

where  $M_1 v_1$  and  $M_2 v_2$  refer to the mass and velocity of the mercury and hydrogen ions respectively. Therefore,

$$v_1/v_2 = \sqrt{M_2/M_1} = T_2/T_1. \quad (3)$$

In the present case  $M_1 = 200.6$  and  $M_2 = 2.016$ . Thus  $T_1 = 10T_2$  approximately.

The ratio  $N_1/N_2$  may be found by taking the ratio  $p_1/p_2$  where  $p_1$  represents the partial pressure of mercury vapor and  $p_2$  that of hydrogen. Hence Eq. (1) may be written in this form

$$V' = \frac{10V_1 + (p_2/p_1)V_2}{10 + (p_2/p_1)}. \quad (4)$$

The values of  $V'$  thus calculated are tabulated in column 3 of Table I. The assumed pressure was .008 mm, which is the vapor pressure of mercury at 46°C. This is about 20° higher than the temperature of the water bath in which the mercury was immersed, but is a reasonable value owing to the heat from the filament.

The calculated values are in fairly good agreement with the observed values, except for higher pressures. This is perhaps due to the effect of increased hydrogen in reducing the amount by which the mercury is warmed by the filament.

*Oscillograph study.* An oscillograph study of the current-voltage characteristics further confirmed the reasonableness of this view. It was observed that when oscillations appeared in the arc of the mixture, there was a tendency for the arc to stay at either the maximum or minimum points for the longer time, depending upon the relative amount of hydrogen present. In general when the pressure of hydrogen was reduced, the oscillations extended in the direction of the lower voltage.

When hydrogen alone was used, no oscillations were observed under varying conditions of pressure and filament temperature and the arc was found to break at 16.2 volts.



When mercury in the trap was kept at room temperature (the actual temperature in the tube as we have explained must have been higher), the arcing characteristics for pressure higher than 0.8 mm were similar to those in pure hydrogen. Below this pressure there were two distinct types of oscillations, one being of greater amplitude and at a higher voltage than the other. Fig. 5A is a schematic diagram illustrating the behavior. It will be noted that the process was reversible.

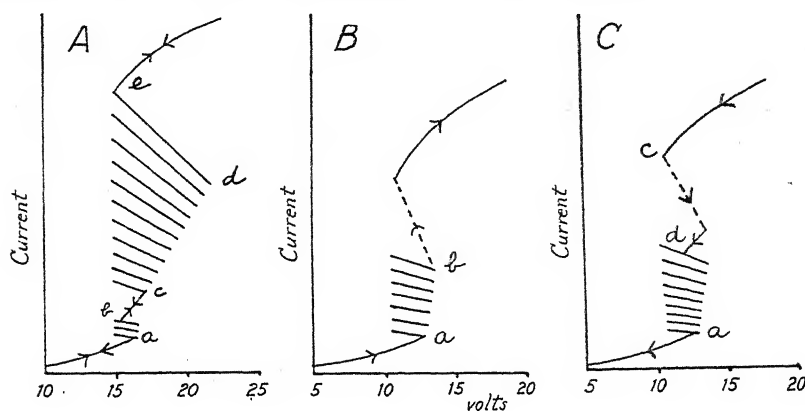


Fig. 5. Types of oscillations in mixtures of mercury vapor and hydrogen.

5A: *a* at 16.5, *b* at 15.3, *c* at 17.2, *d* at 21.8, *e* at 14.5 volts;

5B: *a* at 13.0, *b* at 13.3 volts;

5C: *a* at 13.0, *c* at 10.8, *d* at 12.0 volts.

The oscillations were more difficult to excite when the mercury trap was immersed in the water bath at the boiling point of water (actual temperature much lower of course in the tube owing to condensation in liquid air traps and cool parts of the tube). No oscillations were observed until the hydrogen pressure was reduced to 0.4 mm. The results are tabulated in Table III. The results in the fourth column were calculated

TABLE III

*Arc in mixture of hydrogen with mercury vapor with mercury appendix at 100°C*

Pressure of hydrogen	Striking potential	Breaking potential	
		(observed)	(calculated)
3.0 mm	33.1 volts	16.7 volts	15.5 volts
2.1	31.0	16.0	15.3
1.5	27.3	15.0	15.0
1.1	25.1	14.6	14.7
0.8	20.7	14.1	14.3
0.4		oscillations set in	

from Eq. (4), assuming the pressure of mercury vapor to be 0.4 mm at an assumed bulb temperature of 65°C. Here the larger discrepancies at high



pressures may be attributed to the fact that these pressures are beyond the range in which the arc breaks at the minimum voltage.

Figures 5B and 5C show the type of oscillations which set in at about 0.4 mm with this concentration of mercury vapor. The amplitude of oscillations was evidently larger than in the case of lower concentration and the type that previously appeared at a higher voltage was not present.

In order to account for the peculiar behavior of the oscillations with the two pressures of mercury vapor, let us assume the following cycle of operations. The arc in the mixture was struck only after a sufficient number of hydrogen molecules was ionized under the unfavorable conditions of negative space charge around the filament, since the number of mercury atoms present was always a small fraction of the mixed gases. The increased arc current would now ionize a number of mercury atoms and excite a sufficient number that would dissociate hydrogen molecules by means of "collisions of the second kind," the evidence of which is amply given by the experiments of Cario and Franck,<sup>14</sup> Duffendack and Compton,<sup>12</sup> and Compton and Turner,<sup>15</sup> as well as by the spectroscopic data in this experiment to be presented in the sequel. Both of these effects would further increase the arc current, as was observed. When the voltage was lowered, there might be a sufficient number of positive ions of mercury and of atomic hydrogen effectively to maintain the arc at a lower voltage than in pure hydrogen. However, if these atomic ions could not be sufficiently replaced, as probably would be the case with lower pressure of mercury vapor and therefore less dissociation of the hydrogen molecules, then the current would tend to diminish until the accompanying rise in voltage was enough to again ionize the hydrogen molecules and the cycle was repeated in the form of oscillations.

#### SPECTROSCOPIC OBSERVATIONS ON MERCURY VAPOR AND HYDROGEN

In pure hydrogen the Balmer lines and the secondary spectrum always appeared together, as soon as the arc was struck, with the Balmer lines more intense than the secondary spectrum. This is due, judging by Smyth's conclusions, to the ionization of the hydrogen atoms formed as a result of secondary collisions. Richardson and Tanaka used lower pressures (.2 mm) than those the writer employed (0.4 to 3.0 mm) and succeeded in actually observing the relative absence of the Balmer lines in the region of bluish glow in front of the anode on the side nearest the

<sup>14</sup> Cario and Franck, *Zeits. f. Phys.* 11, 161 (1922).

<sup>15</sup> Compton and Turner, *Phil. Mag.* 48, 360 (1924).

cathode. On the anode side the glow was pink and the Balmer lines were relatively more intense.

In mixtures of mercury vapor and hydrogen, the mercury lines and the Balmer series lines were very much enhanced relative to the secondary spectrum after passing the second arcing potential. We shall further examine this in detail. On the return path of voltage change the mercury as well as the hydrogen lines were visible above the upper break. Only the hydrogen spectrum was observable between the upper and lower breaks. Hg line 5461 showed this effect in a most striking manner. When there was only one striking and one breaking potential, the mercury and the hydrogen lines appeared and disappeared together.

Photographs were taken with the type of arc shown in Fig. 3 at the first and second arcing potentials and at the lowest current point between the two. We shall designate these points *a*, *c*, and *b* respectively. The result of examining the photographs may be summarized thus:

1. The mercury lines 5461, 4358, and 4047 were very faint at *a*, not found at *b*, and very much intensified at *c*.
2. The mercury lines 3650, 3132, 3022, 2967, 2803, 2652, and 2537 were more reduced in intensity relative to the rest of the spectrum at *b* compared with the lines at *a*. They were also very much intensified above the higher break.
3. A number of additional Hg lines including 3367, 3352 and 3343 appeared above the higher break.
4. Most of the secondary spectrum lines were reduced in intensity above the higher break.
5. Bands, probably mercury hydride, at 3572, 3531, 3154 were present at *a* and *b* but disappeared at *c*.
6. A band at 3388 was found at *a* and *b* and disappeared at *c*.

One conclusion seems to be unavoidable from these facts, that between the first and second breaks hydrogen molecules were dissociated into atoms. It is significant to note also that the  $2p$ - $ms$  lines 5461, 4358, 4047 were absent and the  $2p$ - $md$  lines 3132, 3126, 2967, 3022, 2562 and the  $1S$ - $2p$  line 2537 were greatly reduced in intensity at *b*, the lowest current point between the two arcing potentials. It seems reasonable to suppose that excited mercury atoms in the  $2p$  states lost their energy through impact with hydrogen molecules in dissociating them into atoms, as the reduced intensity of the line 2537 would imply that instead of radiating in returning from the  $2p$  state to the normal orbit, the energy of the electrons was absorbed by "collisions of the second kind." Further, it is probable that very few of the mercury atoms were ionized or excited to a higher level than the  $2p$  state owing to a large probability of losing

their energy in this state. This very probably accounts for the reduced intensity of lines corresponding to transitions from the  $s$  or  $d$  states to the  $2p$  states.

In this connection it may be suggested that the two reproducible points of discontinuity above the break of Fig. 4 are probably significant of the process of interchange of energy between the hydrogen and mercury vapor, which is proved by the spectra. No very satisfactory interpretation of them has, however, been made.

The relative intensification of the entire mercury spectrum above the upper break lends further support to our assumption that the mercury atoms were increasingly ionized at this point. From Fig. 3 it will be seen that the difference between the two arcing potentials happened to be exactly 10.4 volts, the ionization potential of mercury atoms. Five independent trials gave about the same value for this difference.

The bands observed at  $a$  and  $b$  are probably mercury hydride bands. They were not observed by Compton and Turner in the positive columns, and the bands observed by them were not detected by the writer; but the origin of the bands in this experiment arose from a region more similar to negative glow than to positive column.

A comparison of the particular lines of the secondary spectrum which were present in a mixture of mercury vapor and hydrogen at the first arcing potential (see Fig. 3) but disappeared at the higher arcing potential leads to the following results. The lines enclosed in brackets were observed after both breaks whereas those without brackets were visible between the two breaks but not above the higher one. 5014, 4930, (4782), 4724, 4684, (4633), (4581), 4555, 4525, 4492, 4449, (4413), (4304), 4254, (4205), (4178), (4158), (4133), 4099, (4064), 3991, 3944, (3890), (3873), (3861), 3804.

This classification has been compared with those based on Zeeman effect, pressure effect, Stark effect and admixture with helium. Unfortunately most of these classifications have not been extensive enough to give a very thorough comparison. In general it may be said that there is no striking agreement between any two of them, a result which emphasizes our ignorance regarding the real origin of the hydrogen secondary spectrum. Unfortunately, the writer did not extend this study to the lines between 5000 and 6400.

When this experiment was in progress, Duffendack published his findings in a similar experiment.<sup>16</sup> He found that practically the entire secondary hydrogen spectrum appeared in full intensity at 15 volts in pure hydrogen and at 14 volts in a mixture of mercury vapor and hydro-

<sup>16</sup> Duffendack, *Astrophys. Jour.* 60, 122 (1924).

gen, and concluded that the spectrum must be due to the neutral molecule, as the potential is distinctly below 16 volts. The writer, while agreeing with the findings of his experiment, is unable to concur in the necessity for his interpretation. Duffendack did not take into consideration initial velocity distribution which amounted in the present experiment to as much as one and one half volts for hot filament temperatures as shown in the "initial voltmeter reading." When this correction is made, the result in pure hydrogen can be adequately explained as being due to the ionization of the molecule. When mercury vapor was present, the increased thermionic current involves an increase in the number of high velocity electrons in the same proportion, and the ionization of the hydrogen molecules apparently can be accomplished at a lower weighted mean voltage. Duffendack's observations with respect to the lowering of the breaking potentials in the arcs of the mixtures are in perfect agreement with our results.

#### ARC CHARACTERISTICS IN MIXTURES OF NITROGEN AND HYDROGEN

Preliminary runs in nitrogen alone confirmed Duffendack's<sup>17</sup> conclusion that the arc broke at about 16 volts, which Smyth by his positive ray experiments<sup>18</sup> has conclusively shown to refer to the ionization potential of the nitrogen molecule. It was found that for maintaining a given thermionic current, the filament need not be as hot as in the case of hydrogen, and the voltage current curve was more nearly reversible. Taking the average of eight runs, the breaking potential of the nitrogen arc was found to be  $16.18 \pm .05$  volts, which is in excellent agreement with Duffendack's value at 16.17 volts.

There is considerable disagreement among the values reported by various investigators for the ionizing potential of nitrogen,<sup>19</sup> ranging between 15.8 and 18 volts. If the breaking voltage for the arc and the ionizing potential of the gas are identical, both Duffendack's and the present results *seem* to place the potential at 16.2 volts, so that within the errors of experiment the ionization potentials for the hydrogen and for the nitrogen molecules seem to be indistinguishable from each other.

The above result is however quite misleading, for when the arcing characteristics were studied by means of the oscillograph, it was found that the lowest voltage at which the arc could be maintained *without oscillations* was 16.9. Below this voltage oscillations set in with an amplitude of about two volts extending in the direction of lower voltage.

<sup>17</sup> Duffendack, Phys. Rev. 20, 665 (1922).

<sup>18</sup> Smyth, Roy. Soc. Proc. A104, 121 (1923).

<sup>19</sup> Consult for instance Duffendack's table, Phys. Rev. 20, 681 (1922).

This accounts for our low value in nitrogen, since the voltmeter reading corresponded to the weighted mean of the high and low peaks of the oscillations.

As in the case of the oscillations in the mixture of mercury vapor and hydrogen, the process of making and breaking the arc was nearly reversible. Fig. 6 is a schematic diagram representing the observations. The oscillations started in at about 17.5 volts or above until the current reached a suitable value and then the arc was maintained at 16.9 volts or above without oscillations. When the voltage was gradually diminished, the oscillations again appeared at 16.9 volts. From eight inde-

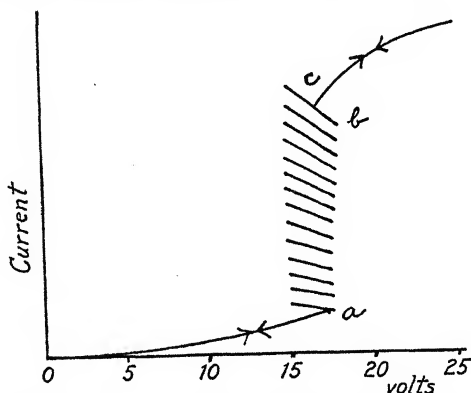


Fig. 6. Oscillations in pure nitrogen; *a* at 17.5, *b* at 18.0, *c* at 16.9 volts.

pendent trials, the point *c* in the figure was located at  $16.90 \pm .07$  volts. Further evidence in support of the 16.9 value for the ionization potential of the nitrogen molecule will be given when we take up oscillations in the mixture of the two gases.<sup>20</sup>

When nitrogen was mixed with hydrogen, the breaking potential of the arc was consistently lowered with the increase of nitrogen until the ratio to hydrogen was unity. Further increase in nitrogen raised the breaking potential again until finally it reached the breaking potential in nitrogen alone as the limit. These points are illustrated in Fig. 7. As in the case of mercury vapor and hydrogen, we again assume that the voltmeter recorded only the mean of oscillations. If this view is correct, we would expect that the points of lowest breaking potential would correspond to

<sup>20</sup> *Note on ionizing potentials.* It should be noted that the values here reported do not include a correction for contact difference of potential between electrodes. Probably the most accurate determinations are those by Mackay (Phil. Mag. **46**, 828, 1923) who referred them to the ionizing potential of mercury as a known standard value. His values for  $H_2$  and  $N_2$  are 15.8 and 16.3 respectively. The present values of 16.2 and 16.9 compare well relatively and suggest a correction of about 0.5 volts.

oscillations of greatest amplitude (in the direction of lower voltage), which the oscillograph showed to be the case.

The oscillograph characteristics, Fig. 8, for the mixtures of the two gases, further strengthened the evidence for fixing the ionization potential

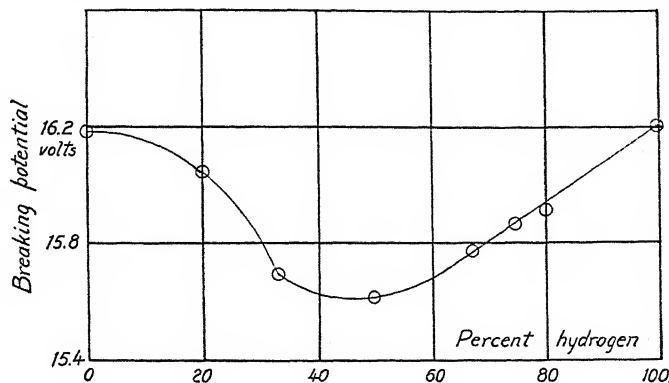


Fig. 7. Breaking potentials in mixtures of  $H_2$  and  $N_2$  in varying proportions.

of nitrogen at about a volt higher than that for the hydrogen molecule. The oscillations of two or three volts amplitude began with the voltmeter reading about 17.0 volts and usually stopped a little below 16.0 volts.

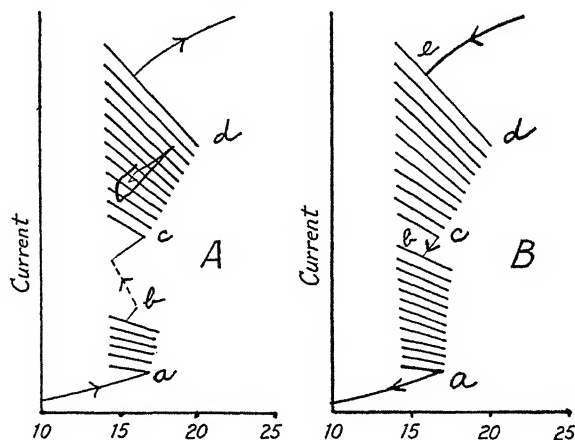


Fig. 8. Oscillations in mixtures of  $H_2$  and  $N_2$ .

8A: *a* at 17.0, *b* at 16.0, *c* at 16.9, *d* at 20.2, or 22.8 volts.

8B: *e* at 16.2 volts; other values same as in 8A.

(The decrease in voltage was due to the increase in the arc current of course.) On reaching 16.0 volts, the current increased with a sudden jump and the voltage correspondingly lowered. When the potential was further increased to 16.9 volts, the oscillations started again with a



larger amplitude with its maximum at about 20 or 22.5 volts. Higher filament temperature and excess of hydrogen seemed to favor the higher voltage. When the path was reversed the oscillations came in at 16.2 volts, stopped at 16.9 volts, began again at 16.0 volts, and finally stopped altogether at 17.0 volts, the very point where the oscillations set in in the direction of increasing voltage. This characteristic of reversibility has also been found in mercury<sup>21</sup> and in helium<sup>22</sup> for both of which oscillations have been observed in the low voltage arc.

It seems plausible to account for these phenomena as follows. It is known that the "efficiency" of ionization is much greater in nitrogen than in hydrogen. Thus, at the striking point *a* it is the nitrogen ions which are chiefly responsible for the neutralization of space charge, in spite of the higher ionizing potential of nitrogen. At the breaking point *e*, on the other hand, the electron emission is so great that the necessary amount of ionization can be obtained from the hydrogen. Thus the striking voltage *a* is characteristic of nitrogen and the breaking voltage *e* of hydrogen. It should be noted that the oscillations always set in with increasing current at 16.9 volts (nitrogen) rather than the 16.2 volts (hydrogen) in agreement with the fact that they could be found in pure nitrogen but not in pure hydrogen.

At pressures higher than 1 mm, when there was an excess of hydrogen and when the filament temperature was moderate, there were usually two striking and two breaking potentials, as is shown in Fig. 9. These breaks were accompanied by oscillations and the value of the second striking potential was also determined by means of an oscillograph by observing the maximum peaks in the higher voltage oscillations. The calibration did not give readings more accurately than within half of a volt. The average for 21 trials was 22.7 volts. This agrees unexpectedly well with the result from direct voltmeter reading.

It is not easy to decide just what this potential stands for. Horton and Davis<sup>23</sup> located a critical potential for hydrogen at 22.8 volts, and they attributed it to the ionization of the hydrogen molecule. Brandt<sup>24</sup> and Bazzoni and Waldie<sup>25</sup> observed a critical potential near this value (25.4 volts) in nitrogen. Finally, Smyth observed a critical potential in nitrogen at  $24.1 \pm 1.0$  volts at which doubly charged atomic ions appeared. We shall see that the spectroscopic data suggest that this is

<sup>21</sup> Y. T. Yao, *Phys. Rev.* **21**, 1 (1923).

<sup>22</sup> Compton, Lilly and Olmstead, *Phys. Rev.* **16**, 282 (1920).

<sup>23</sup> Horton and Davis, *Phil. Mag.* **26**, 872 (1923).

<sup>24</sup> Brandt, *Zeits. f. Phys.* **8**, 32 (1921).

<sup>25</sup> Bazzoni and Waldie, *Jour. Frank. Inst.* **197**, 57 (1924).



actually a critical potential of nitrogen. Probably the reason for not detecting it in pure nitrogen is that the currents in the latter case were so large that additional effects associated with the second critical potential were masked.

#### SPECTROSCOPIC OBSERVATIONS IN NITROGEN AND HYDROGEN

There are three bands usually associated with the spectrum of ammonia; the ultraviolet band between 3295 and 3432Å, the Schuster bands at 5635 and 5682Å and the alpha band which extends throughout the greater part of the visible spectrum.

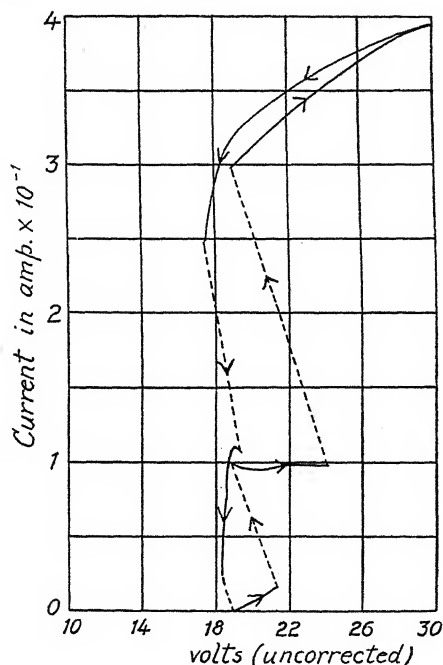


Fig. 9. The two striking potentials in mixtures of  $H_2$  and  $N_2$ .

Over ten years ago E. P. Lewis<sup>26</sup> found in vacuum tube experiments that the above mentioned ultraviolet band was present in a mixture of hydrogen and nitrogen with all proportions of the two gases, whereas in each gas alone this band was not found. At the time he attributed it to ammonia. More recently Fowler and Gregory<sup>27</sup> took very precise measurements of the wave-lengths of this band and arranged them into seven series according to their frequency differences. They found by comparison that the ultraviolet band is represented in the solar spectrum.

<sup>26</sup> E. P. Lewis, *Astrophys. Jour.* 40, 154 (1914).

<sup>27</sup> Fowler and Gregory, *Phil. Trans.* A218, 351 (1919).

Bair<sup>28</sup> studied the ammonia spectrum by means of transformer discharges and found that the ultraviolet band appeared when the gas was flowing but not when it was at rest. He reported also that the insertion of a small capacity increased the intensity of the band when the gas was at rest and that "mixtures of flowing ammonia and oxygen gave the ultraviolet band with uncondensed discharge." Still more recently W. B. Rimmer<sup>29</sup> measured the more prominent lines of the alpha band and studied the appearance of the various bands under a variety of experimental conditions. He found (1) "no record of the existence of the Schuster bands in the ammonia flame"; (2) "the Schuster bands have given no sign of resolution under high dispersion," and (3) "the effect of a condensed discharge seemed to be to increase the intensity of the ultraviolet band with respect to the Schuster bands."

Rimmer summarized the conclusions reached by the various investigators and his own as follows: "Lewis suggested (corroborated by Barratt and Bair) that the Schuster bands probably represent the true spectrum of ammonia and that the ultraviolet band is probably due to another emission center arising from a more stable combination of N and H other than the normal molecule of ammonia. In addition the present investigation (Rimmer's own work) suggests that the alpha band is due to an emission center which represents a first stage of dissociation of the normal ammonia molecule into more stable forms and the ultraviolet band to an emission center which represents a still more advanced stage of dissociation into constituent atoms."

The writer in studying the spectra in the low voltage arc obtained results similar to those observed by Lewis, namely, that the ultraviolet band was present in the mixtures of the two gases in all proportions but not in each gas alone. The least amount of nitrogen in the presence of hydrogen would cause the appearance of this band. In fact the writer had considerable difficulty in getting rid of this band after the mixture was tried in the tube. When ammonia either wet and dried was used instead of the mixtures, the same band was observable after the arc was struck at about 20 volts.

This ultraviolet band was observable as soon as the arc was struck at about 17 volts, provided there was only one arcing potential observable, and its intensity increased rapidly. It was distinctly observable at between 20 and 25 volts. In such cases, the oscillographs showed that the maximum peaks of oscillations were at about 22 or 23 volts. Under conditions where there were two striking and two breaking potentials,

<sup>28</sup> Bair, *Astrophys. Jour.* 52, 301 (1920).

<sup>29</sup> Rimmer, *Roy. Soc. Proc. A*103, 696 (1923).

the ultraviolet band appeared only with the second striking potential, estimated at 22.8 volts, whereas before the second jump, the band was entirely invisible. If the voltage was diminished after passing the second striking potential, faint traces of the band could be seen as low as the first breaking potential at about 15.5 volts. We shall assume that the 22.8 volt potential is responsible for the excitation of the ultraviolet band.

In accordance with the quantum theory of band spectra, the writer has employed Fowler and Gregory's measurements in calculating the moment of inertia of the corresponding molecule based upon the relationship  $\Delta\nu = h/4\pi^2 I$ , where  $h$  is the Planck constant,  $\Delta\nu$  the frequency difference, and  $I$  the moment of inertia of the molecule. Taking the wave-number difference to be 28.5,  $I$  comes out to be  $1.95(10)^{-40}$  gm cm<sup>2</sup>. This is well within the range of values attributed to the ammonia molecule from measurements of the infrared absorption spectrum of ammonia. Schierkolk<sup>30</sup> found two values: (1) From the band at  $10.5\mu$ ,  $I$  was found to be  $1.48(10)^{-40}$  gm cm<sup>2</sup>; and (2) from the band at  $6.1\mu$ ,  $I = 2.72(10)^{-40}$  gm cm<sup>2</sup>. The difference in these two values Schierkolk attributed to the different orientation of the ammonia molecule. The writer also calculated the moment of inertia from B. J. Spence's<sup>31</sup> measurements of the absorption spectrum at  $3\mu$ . Taking the average  $\Delta\nu = C \times 19.5$ ,  $I$  would be  $2.83(10)^{-40}$  gm cm<sup>2</sup>, which is in agreement with Schierkolk's higher value within errors of experiment.

Taking the moment of inertia as  $2.8(10)^{-40}$  gm cm<sup>2</sup>, if we assume a model for NH in which a nitrogen nucleus and a hydrogen nucleus rotate around their center of mass, the distance between the nuclei is  $1.17(10)^{-8}$  cm. If a model for NH<sub>2</sub> were assumed in which the heavy nitrogen nucleus is located at the center of mass and a hydrogen nucleus symmetrically placed on each side, the distance between the hydrogen nuclei would be  $1.54(10)^{-8}$  cm. Finally, if we assumed a model for NH<sub>3</sub> to be such that the nitrogen nucleus is situated at the center of a circle in which an equilateral triangle is inscribed at whose vertices the hydrogen nuclei are located, the diameter of such a circle is  $1.25(10)^{-8}$  cm. All three values agree reasonably with kinetic theory predictions and therefore, with our present knowledge about molecular arrangements, we cannot decide which of the three types of molecules is responsible for the band. The one conclusion which we can draw is that the *molecule cannot contain more than one atom of nitrogen*. If two atoms of nitrogen were present in such a molecule, the molecular diameter would have to be of the order of  $(10)^{-9}$  cm. We therefore conclude that at 22.8 volts some atomic

<sup>30</sup> Schierkolk, Zeits. f. Phys. 29, 277 (1924).

<sup>31</sup> Spence, Jour. Opt. Soc. Amer. & R.S.I. 2, 127 (1925).

nitrogen ions must be present and this is well supported by Smyth's positive ray experiments in which doubly charged atomic ions were found at this potential.

Now to come back to the origin of the 22.8 volt break. In the light of the above discussion we must attribute it to nitrogen and as we shall see later to a production of atomic ions of nitrogen, in all probability. For ionized molecules and atoms (formed by secondary collisions and dissociation due to the filament) of hydrogen were in abundance at the first arcing potential whereas atomic nitrogen ions have never been observed below 22.8 volts. In further support of this view, the negative band of nitrogen at 3914 was observed to come out simultaneously with the ultraviolet band of ammonia and with the appearance of a line. Possibly this is due to a process related to the dissociation of the nitrogen molecule into atomic ions. L. and E. Bloch<sup>32</sup> also observed the appearance of this band at about 22.5 volts.

The so-called Schuster bands, between 5635 and 5822 were entirely absent from the spectrum in the mixtures of the two gases as long as the last trace of water vapor was condensed in the liquid air traps; but when the liquid air flasks were taken away, in three out of four instances, with a different filament each time, the Schuster bands were unmistakably present when the light from a point very near the target was examined. The failure to observe the bands during one of the trials is attributed to the insufficient amount of water vapor present and to the comparatively short distance between the electrodes which made the combination of atoms into more complicated molecules difficult. The writer feels certain that the bands were not due to any material coming out of the target, for in every trial with dry gases, the Schuster and alpha bands were absent when the light from the same part of the arc was focussed on the spectrometer slit.

Thus far our experiment does not tell us whether water vapor or mercury vapor was responsible for the bands. To test this point a few drops of mercury were put in the attached tube and the traps were again immersed in liquid air. We are now sure that mercury vapor alone was present. The Schuster bands were still missing in the spectrum.

Ammonia prepared by evaporation from concentrated solution and stored over potassium hydroxide sticks was next admitted into the system. Well dried gas showed no trace of the Schuster bands. When either water vapor or oxygen in small amount was mixed with it, the Schuster bands invariably came out. The filament at this stage, as would be expected, burnt out very rapidly.

<sup>32</sup> L. and E. Bloch, *Comptes Rendus*, 175, 225 (1921).

A further point of interest is the fact that the Schuster bands appeared only when the potential was raised to 70 volts or over, which in Duffendack's experiments was the critical potential for the formation of "active nitrogen."

In the light of these facts, the writer is not able to concur with Rimmer and Bair as to the origin of these bands, namely that the Schuster bands originate from the normal ammonia molecules and the ultraviolet band belongs to a more stable combination of N and H, possibly other than ammonia. The test in dry ammonia with and without a small oxygen content seems conclusive with respect to this point.

Moreover, if these bands were due to ammonia, the high voltage at which these bands appeared would not harmonize with the experiments of Andersen and of Storch and Olson, who found that ammonia was produced at the striking of the arc. The potential difference cannot be accounted for by any theory of secondary collisions.

A study of the conditions under which the Schuster bands have been previously observed unmistakably supports the writer's point of view. Schuster,<sup>33</sup> the discoverer of these bands, observed them for the first time when he introduced "a few drops of a strong solution in water" into the vacuum tube and the discharge was passed while the tube was being evacuated. Lewis and Bair maintained the visible bands only when a continuous stream was allowed to pass through the tube. Under such conditions traces of water vapor were likely to be present. Rimmer's best results were obtained when he evaporated ammonia from a strong solution, employing a water pump for evacuation. In general these experiments did not show that water vapor was not present.

The writer therefore ventures to suggest that the Schuster bands are due to a heavy molecule containing atoms of hydrogen, nitrogen and oxygen, possibly  $\text{NH}_4\text{OH}$ , which is extremely unstable and can be formed only when there are nitrogen atoms in a highly excited state such as are obtainable at 70 volts in the low voltage arc. This type of molecule will explain some of Rimmer's observations and account for the unresolved character of the band as due to its large moment of inertia. Then too, we would not expect these bands to be present under conditions of low excitation such as in the oxygen flame.

The above analysis suggest as a consequence that the ultraviolet band originates from the anhydrous ammonia molecule itself. Since there were no other bands observable in dry mixtures of nitrogen and hydrogen up to 120 volts in addition to the hydrogen and nitrogen

<sup>33</sup> Schuster, Report British Association (1872).

spectra, although ammonia is formed, it is reasonable to attribute it to ammonia rather than to  $\text{NH}$  or  $\text{NH}_2$  which up to the present have not been observed as temporary products of such arcs.

Perhaps a question may be raised in reference to Storch and Olson's experiments in which they found that ammonia was formed as soon as the arc was struck whereas in our experiment the ultraviolet band is associated with 22.8 volts. There are two possible answers to such an objection. In the first place it is possible that  $\text{N}_2\text{H}_6$  molecules may be formed which finally dissociate into  $\text{NH}_3$  molecules. Such a process would, of course, be much less probable than the direct formation of ammonia at 22.8 volts and may account for the marked increase in the rate of reaction at 23 volts in all of the curves that were published by Storch and Olson. The coincidence of the first and most distinct jump after the arcing potential in the curves of these authors with our 22.8 volt potential is probably not accidental. In the second place, the discrepancy may be due to a difference in the sensitivity of the two methods of detection.

In conclusion, the writer takes this opportunity to express his sincere thanks and grateful appreciation to Professor K. T. Compton for suggesting this problem and for his constant guidance and inspiration throughout this investigation. He acknowledges also with pleasure his indebtedness to Mr. C. C. Van Voorhis and Dr. L. A. Turner for their help in several matters of technique.

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ON A CLASS OF ONE-VALENCE-ELECTRON EMITTERS  
OF BAND SPECTRA

BY ROBERT S. MULLIKEN\*

## ABSTRACT

Bands emitted by one-valence-electron molecules.—*Series A:* BeF, BO, CO<sup>+</sup>, CN, N<sub>2</sub><sup>+</sup>. These molecules each contain, like the Na atom, 8+1 electrons outside the nuclei and K electrons. The bands of CO<sup>+</sup> (the comet-tail, negative Deslandres and new quadruple-headed bands reported by Baldet and Johnson) are particularly discussed and analogies to the bands of BO and of CN are pointed out, as well as analogies between the bands of N<sub>2</sub><sup>+</sup> and of CN. The data for BeF bands are less complete. The lines of the known band systems of all these molecules can in each case be expressed as combinations of three electronic terms (each of course with a variety of vibrational and rotational states). These are a singlet term *N* probably belonging to the normal state, a doublet term *A* corresponding to the first excited state, and a singlet term *B* corresponding to the second excited state. There is evidence that the average angular momentum of the emitting electron—which is presumably the odd ninth electron—is the same for the *N* and *B* states, but different for the doublet *A* state; presumably the former resemble *s* states, the latter resemble (inverted doublet) *p* states. In the cases of BO and CO<sup>+</sup>, all of the three conceivable combinations between *N*, *A*, and *B* are known; two are known in the case of CN, and one in that of N<sub>2</sub><sup>+</sup>; the systems not yet observed probably lie in the infrared. There is a remarkable parallelism between the spectra of the several molecules mentioned in respect to structure of analogous band systems and to molecular constants of corresponding electronic states (cf Table I). *Series B:* MgF, AlO, SiN. These molecules contain an additional electron shell. They are the probable emitters of band spectra which show marked analogies to those of BeF, BO and CN. *Additional series* of emitters are represented by CaCl, SrBr, etc.

Suggested grouping of bands according to the number of valence electrons of the emitters.—Molecules with no unused valence electrons—HF, LiF, BN, NaCl, etc.—show analogy to the rare gases; they do not emit electronic band spectra. Molecules with two excess electrons—CO, NO<sup>+</sup>, N<sub>2</sub>, SiO—should show analogies to alkaline earth metals. The odd multiplicity of N<sub>2</sub> agrees with this suggestion. Molecules with three excess electrons, e.g., NO, should resemble Al; in fact the bands probably due to NO show even multiplicity.

Nature of multiplicity in band spectra.—Two causes of multiplicity are suggested: (a) connected with the interaction of the emitting electron with the rest of the molecule, and (b) attributed by Kratzer to the interaction of the angular momentum of the emitting and other electrons with that of the nuclei. Examples of each are discussed.

Emitters of certain bands.—*Second negative N<sub>2</sub> bands of Duffendack* may be due to neutral nitrogen molecules in each of which two electrons are initially excited. Evidence is presented for attributing the familiar *aluminum bands* to AlO.

\* National Research Fellow.



IN previous papers<sup>1,2</sup> attention has been called to a class of alkali-metal-like diatomic "odd molecules" containing one easily excited electron, and giving rise to conspicuous band spectra. These molecules do not appear in ordinary chemistry, doubtless on account of the activity of this odd electron. Except for the odd electron, these molecules have just enough electrons to form one or more rare gas shells. From the elements of the first and second series of the periodic system the following two series of such molecules are possible:

Series A:	Li	BeF	BO	CN
Series B:	Na	MgF	AlO	SiN

In each case the positive valence of the more electropositive atom exceeds by one the negative valence of the other atom, thus leaving one of the former's valence electrons free as in an alkali metal atom. Numerous additional examples of this type are possible with homologous elements of higher atomic weight; some of these (of which CaCl is typical) have been previously discussed.<sup>2</sup> Such ionized molecules as  $\text{CO}^+$  and  $\text{N}_2^+$  also belong with series A. The spectra of the compounds of this type, like those of the alkali metals, show the presence of electronic doublets. Series A differs from B or other possible series in that the total number of electrons is sufficient only for one group of eight, so that, as was suggested previously,<sup>1</sup> it may be that the two nuclei share an octet and that, at least when the nuclear charges are nearly equal, the molecule as a whole specifically resembles a Na atom. The electropositive atoms in the molecules of series A and B and similar series might also be considered, at least for the earlier members of each series, as "stripped atoms" whose lost electrons, however, now attached to the electronegative atom, still exert a considerable screening effect.

The chief object of the present paper is to bring together evidence that the molecules of series A and B are indeed all ready emitters of band spectra, and to show from these spectra, so far as is possible with the data available, that these molecules are closely similar to one another in many respects. This will be preceded by a brief discussion of the question of multiplets in band spectra.

#### MULTIPLICITY IN BAND SPECTRA

Mecke<sup>3</sup> has recently discussed the question of multiplets in band spectra and has attempted to set up a formal analogy to the relations

<sup>1</sup> R. S. Mulliken, *Phys. Rev.* **25**, 259-294 (1925), especially pp. 290-1.

<sup>2</sup> R. S. Mulliken, *Phys. Rev.* **26**, 1-32 (1925), especially pp. 29-32.

<sup>3</sup> R. Mecke, *Zeits. f. Phys.* **28**, 261-77 (1924).

which hold in line spectra. He assumes the angular momentum of the emitting electron and of the nuclei, in molecules, to be respectively analogous, in determining multiplet structure, to the angular momentum of core and of emitting electron in atoms. But it seems to the present writer that the real situation must be more complicated, and that there should be two distinct causes of multiplicity in band spectra, (a) one connected with the interaction of the emitting electron with the rest of the molecule, as in the case of excited electron and atom-core in line spectra, and (b) another which has been attributed by Kratzer<sup>4</sup> to the interaction of the angular momentum of the emitting and other electrons with that of the nuclei. Cause (a) gives the most obvious explanation of the occurrence of systems of bands having true multiple origins and two or more widely-spaced heads for each band, separated by a frequency-interval which remains constant or nearly so throughout the spectrum. In the following this will be called multiplicity of class *a*. Examples of this are the doublet  $\alpha$  bands of BO ( $\Delta\nu=126$ ), the interesting doublet alkaline earth halide bands,<sup>2</sup> the doublet  $\beta$  ( $\Delta\nu=87$ ) and  $\gamma$  ( $\Delta\nu=\text{about } 111$ ) bands of NO, the red CN bands ( $\Delta\nu=\text{about } 54$ ) and, particularly striking because the structure has been analyzed in detail, the doublet bands of CO<sup>+</sup> ( $\Delta\nu=126$ ). Except in the  $\beta$  bands of NO, each doublet component or sub-band has two heads ( $\Delta\nu=13$  for BO and about 13 for CO<sup>+</sup> and 19 for NO $\gamma$ ), giving an apparent quadruplet structure. But Baldet's work<sup>5</sup> on the comet-tail bands of CO<sup>+</sup> shows that here the two heads belong to a Q and an R branch, respectively, and it is probable (contrary to the assumption made in previous papers<sup>1,2</sup> in the cases of BO and the alkaline earth halides) that the *small*  $\Delta\nu$  is not an electronic doublet in any of the above cases. The cuprous halides<sup>2</sup> show possible further examples of class (a), differing, however, from the above cases, as might be expected from the much larger  $\Delta\nu$  values, in that the molecular constants (vibration frequency, etc.) differ considerably for the various initial electronic states comprising the multiplet.

An apparently distinct type of multiplicity in band spectra, which will here be called *b*, is the "fine structure," according to the nature of which bands have been classed by Heurlinger as singlet, doublet, and triplet bands.<sup>6</sup> Singlet bands may consist of single lines or of doublets whose separation increases steadily with the rotational quantum number, from

<sup>4</sup> A. Kratzer, (a) Ann. der Phys. 71, 72 (1923); (b) Zeit. f. Phys. 16, 353 (1923); (c) 23, 298 (1924); (d) Naturwissenschaften 27, 581 (1923).

<sup>5</sup> F. Baldet, Compt. Rend. 180, 820 (1925).

<sup>6</sup> T. Heurlinger, Dissertation, Lund 1918. Cf also review by R. Mecke,<sup>23</sup> who gives an excellent description and diagrams of the various types of fine-structure multiplets.

zero or nearly so at the origin; the violet CN bands are an example of the latter type. Heurlinger doublet and triplet bands have relatively wide separations near the origin, but the components approach each other with increase in the rotational quantum number; each component may in addition show doublet structure of the violet CN type. The structure of Heurlinger singlet and doublet bands has been explained by Kratzer in terms of cause *b*; but there are difficulties,<sup>7</sup> especially in the case of triplet bands,<sup>3</sup> and it may be that class *a* and class *b* multiplicity are not wholly distinct except as limiting cases. Causes *a* and *b* should in general both operate, it would seem, to produce whatever complexity is observed.

#### ANALOGY BETWEEN THE BANDS OF CO<sup>+</sup>, BO, CN AND N<sub>2</sub><sup>+</sup>

Let us now turn to a detailed consideration of the molecules of series A and B. The so-called comet tail bands and the first negative carbon bands of Deslandres are always obtained together and have been attributed to CO by nearly all who have studied them,<sup>8,9,10,11</sup> in particular, Baldet has obtained them in pure CO.<sup>11</sup> Recently it has been found<sup>12,13</sup> that these two systems of bands have a common final electronic state. They are obtained at very low pressures, or near the cathode at somewhat higher pressures<sup>9</sup>—conditions where ionization is to be expected. Under similar conditions Baldet<sup>11</sup> obtains the N<sub>2</sub><sup>+</sup> (negative nitrogen) bands when a little N<sub>2</sub> is introduced. They are also obtained when traces of carbon compounds are added to helium at 20 mm pressure; perhaps here the excitation occurs in impacts with metastable excited He atoms whose energy (about 20 volts) is approximately that required to simultaneously ionize and excite the CO molecule so as to give rise to the emission of these bands. Under similar conditions,<sup>10</sup> traces of N<sub>2</sub> give the N<sub>2</sub><sup>+</sup> bands. The above facts, together with the extraordinary analogy which these systems of bands present to the *α* and *β* bands of BO,<sup>1</sup> make it practically certain that they are due to the CO<sup>+</sup> molecule, which has

<sup>7</sup> R. T. Birge, Phys. Rev. **25**, 240 (1925) (abstract No. 21).

<sup>8</sup> A. Fowler, Month. Not. Roy. Astron. Soc. **70**, 176 (1909); **70**, 484 (1910); Astrophys. J. **35**, 85 (1912); and earlier work of Deslandres.

<sup>9</sup> P. R. Merton, and R. C. Johnson, Proc. Roy. Soc. **103A**, 383 (1923).

H. B. Lemon, Proc. Nat. Acad. Sci. **11**, 41 (1925). Cf also W. Jevons, Phil. Mag. (6), **47**, 586 (1924), in regard to the Deslandres bands.

<sup>10</sup> R. C. Johnson, Proc. Roy. Soc. **108A**, 343 (1925).

<sup>11</sup> F. Baldet, Compt. Rend. **178**, 1525 (1924); **180**, 271, 1201 (1925).

<sup>12</sup> C. M. Blackburn, Phys. Rev. **25**, 888, 1925 (abstract); other preliminary results, Proc. Nat. Acad. Sci. **11**, 28 (1925); and unpublished work.

<sup>13</sup> R. T. Birge, Nature, **116**, 171 (Aug. 1, 1925)

the same number of electrons as BO, presumably arranged in a very similar manner.

*Analogy of CO<sup>+</sup> to BO bands.* The quadruple-headed comet-tail bands in the visible are clearly analogous to the  $\alpha$  bands of BO; the identical values of  $\Delta\nu$  (cf above) in the two cases are particularly striking. Preliminary results of an analysis of these bands have been given by Blackburn<sup>12</sup> and by Baldet<sup>5</sup>; they show that each comet-tail band consists of two closely similar sub-bands which are nearly superposable by a translation of about 126 units along the wave-number axis, thus clearly constituting a class (a) doublet. Blackburn's analysis of the CO<sup>+</sup> bands, which he has kindly rendered available to the writer before publication, shows that the lines can all be expressed as the difference of two sets of terms of the form:

Initial:  $F_i'(n', m') = \nu_i^e + F'(n') + B_i' n' m'^2 + \dots$  ( $m'$  = nearly integral.)

Final:  $F''(n'', m'') = F''(n'') + B'' n'' m''^2 + \dots$  ( $m''$  = half-integral).

Here  $F(n) = an - bn^2 + \dots$ ,  $n$  being the vibrational quantum number, while  $m$  is the nuclear rotational quantum number. For the two sub-bands,  $\nu_i^e$  differs as already indicated,  $F'(n')$  is nearly if not quite identical, while  $B_i'$  differs slightly. As shown by Baldet,<sup>5</sup> each sub-band consists of a P, a Q, and an R branch, the latter two giving the two observed heads. Baldet also finds a second intense Q branch (Q' branch), which is apparently absent under the conditions used by Blackburn. If in the latter case the direct excitation of the CO is by excited He atoms, the situation may parallel that of the  $\beta$  bands of BO as excited in the arc and in active nitrogen.<sup>1</sup> In the arc the  $\beta$  bands show a doublet structure, while in active nitrogen one component of each doublet is missing.

The single-headed ultraviolet first negative Deslandres' bands, as studied by Blackburn, show marked analogy to the  $\beta$  bands of BO. The data on these bands are not such as to permit a wholly independent analysis, but on the very probable assumption that, in view of the identity of  $F''(n)$  for the two systems,<sup>10,11</sup>  $F''(n'', m'')$  is identical for the two, the analysis shows that  $\Delta m = \pm 1$ , hence that  $m'$ , like  $m''$ , has half-integral values—all quite as in the violet CN bands. Hence the Deslandres' bands probably consist of normal P and R branches of the violet CN type, except for the apparent absence of the class (b) doublets which are characteristic of the latter.

In addition to the two systems of CO<sup>+</sup> bands above discussed, which, like the  $\alpha$  and  $\beta$  systems of BO, are both shaded toward the red, some additional quadruple-headed bands which are shaded toward the violet

have been reported by Baldet<sup>11</sup> and by Johnson.<sup>10</sup> They have the same major doublet separation ( $\Delta\nu=126$ ) as the comet-tail bands, although the minor doublet separation ( $\Delta\nu=25$ , according to Johnson) is different. A study of the data shows that they form a system having for their initial electronic state the initial state of the negative Deslandres' bands, and for their *final* electronic state the *initial* state of the comet-tail bands; on this basis the bands observed by Baldet have the vibrational quantum numbers  $(n', n'') = (0, 1)$ ,  $(0, 0)$ , and  $(1, 0)$ , while the bands observed by Johnson correspond to  $(0, 1)$ ,  $(1, 2)$ ,  $(0, 0)$ ,  $(1, 0)$ ,  $(2, 0)$ , and  $(3, 0)$ —except that the absolute  $n''$  values are subject to the same uncertainty which is present in the  $n'$  values for the comet-tail bands (cf note to Table I). The fact that the bands are shaded toward the violet follows at once from the analysis of the other two systems as discussed in the preceding paragraphs, for according to this  $B$  is greater (see Table I) for the initial state of the Deslandres' bands than for that of the comet-tail bands, hence  $C (=B' - B'')$  is here positive. The different minor doublet separation is also to be expected; the structure of the bands is presumably of the P, Q, R type, like the comet-tail bands, but with the P and Q, instead of the Q and R branches, forming heads. This third system of  $\text{CO}^+$  bands is evidently completely analogous to the "combination system" of BO bands,<sup>1</sup> except for the probably superficial difference that only the Q heads are conspicuous in the latter.

Table I summarizes the molecular constants determined by the analysis of the  $\text{CO}^+$  bands. Comparative data are also given on BO. From the close analogy to  $\text{CO}^+$  it is now probable that the four heads ( $A_1, A_2, B_1, B_2$ ) of the  $\alpha$  bands of BO are R and Q heads ( $R_A, Q_A, R_B, Q_B$ , respectively) corresponding to a double electronic level, and not R heads corresponding to a quadruple level, as previously<sup>1</sup> assumed. Considerable independent support is given to this conclusion by the previously somewhat mysterious fact that the combination bands of BO (ref. 1, pp. 284-7) each show only two strong heads instead of four. These strong heads are no doubt the beginnings of Q branches (it may be noted that the Q heads are more intense than the R heads in the  $\alpha$  bands); P and R branches may well also be present, the former giving rise to heads, but evidently of low intensity since their presence was not detected except perhaps in one or two cases. The positions of the heads of the combination bands can furthermore be correctly calculated, as should be possible on the above basis, by subtracting observed positions of  $Q_A$  and  $Q_B$   $\alpha$  heads from calculated positions of suitable  $\beta$  band-origins. In spite of the changed interpretation of the bands, no change is required in the values of  $B'$  and  $B''$  previously given, nor in the interpretation of the  $\beta$



bands, nor in other essential results (such as the existence of half-integral vibrational quantum numbers) of the discussion previously given.

*Analogy to CN bands.* It is probable that there is a more or less complete analogy between the comet tail and Deslandres' bands of  $\text{CO}^+$ , the  $\alpha$  and  $\beta$  bands of BO, and the red and violet CN bands. The doublet structure and quadruple heads of the comet tail bands and the  $\alpha$  bands of BO again appear in the red CN bands; in all three cases the doublet component of longer wave-length is the more intense, as if due to an *inverted* pair of  $p$ -terms for the initial state. In each case the larger doublet separation is more or less variable; in BO, slight variability was reported by Jevons, although not noted by the present writer<sup>1</sup>; in  $\text{CO}^+$ , Baldet reports a change from  $\Delta\nu$  = about 17 at  $\nu$  = 18,000 to about 10 near  $\nu$  = 31,000; in CN (for data of Kayser-Konen, Handbuch der Spektroskopie, Vol. VII), the smaller  $\Delta\nu$  changes for the low-frequency pair of heads in each band from about 18 near 14700 to 15 near 21000, and from about 28 to about 21 in the same range for the high-frequency pair, the head of highest frequency also being unusually weak (probably because it corresponds to a relatively high rotational quantum number). This evidence points strongly to a close resemblance in structure for the  $\alpha$  BO and the red CN bands to the P, Q, R comet-tail type, with its true doublets (large, constant  $\Delta\nu$ ), and its false doublets (small, variable  $\Delta\nu$ ) corresponding to the separation between a Q and an R head; the marked inequality of the two small  $\Delta\nu$ 's in CN may be attributed to an unusually large difference in the values of  $B'$  for the two components of the true doublet, combined with a relatively small value of  $C(C = B' - B'')$ .

*Discussion of electronic states of the molecules.* The above analogies are present to a marked degree in the  $F(n')$  and  $F''(n'')$  coefficients and in the values of  $\nu^e$ , as is shown in Table I, which summarizes the available data from the band spectra of the molecules of series A and B. These coefficients, it may also be noted, vary in a more or less systematic manner with the atomic number or weight. The values of the vibration frequency ( $\alpha'$ ) and of the moment of inertia (equal to  $h/8\pi^2 B'$ ) suggest in each case a markedly lesser stability of the molecule for the *first* than for the *second excited state* of the molecule in spite of the smaller energy of electronic excitation in the former. Apparently the motion of the excited electron is of a quite different type for the two excited states, and furthermore differs less in the second than in the first excited state from that in the common final, probably normal, state. This is understandable in terms of Kratzer's interpretation<sup>4</sup> of bands for which  $\Delta m \neq \pm 1$  or 0. Such bands are explained by postulating that the resultant electronic angular momentum changes in such a way that  $\Delta j = \pm 1$  or 0,

where  $j$  is the quantum number corresponding to the *total* angular momentum (analogous to the inner quantum number in line spectra), and here equal to the vector sum of the electronic and nuclear rotational quantum numbers  $\rho$  and  $m$ . In case the latter two are parallel,  $\Delta j = \Delta m + \Delta \rho = \pm 1$  or 0. In the comet tail bands, where  $\Delta m$  is not equal to 0 or  $\pm 1$  (and presumably by analogy in the red CN and  $\alpha$  BO bands)  $\Delta \rho$  must certainly differ from zero if  $\Delta j = \pm 1$ , 0, whereas in the Deslandres and violet CN bands—and presumably in the  $\beta$  BO bands—with  $\Delta m = \pm 1$ , the simplest assumption is  $\Delta \rho = 0$ . The simplest explanation of the latter ( $\Delta \rho = 0$ ) is that the average angular momentum of the *emitting electron*—which in the case of odd molecules of the CN type is presumably the “odd” electron and presumably is the *only* electron whose quantum numbers here change—does *not* change during emission (cf Kratzer,<sup>14</sup> p. 83) but that in the former ( $\Delta \rho \neq 0$ ) its angular momentum *does* change in direction if not in magnitude. The relations mentioned above between the characteristics of the molecule in its different electronic states may then be correlated with the average angular momentum (and perhaps with an azimuthal quantum number) of the emitting electron. Furthermore, the presence of class *a* doublets for the *first excited* state in these molecules, and their absence in the *normal* and in the *second excited* state, are now explained if the two latter, which have *the same*  $\rho$ , are of the nature of *s* states, while the former, which has a *different*  $\rho$ , is of the nature of an inverted doublet *p*-state. (This is of course contrary to a suggestion made in a previous paper<sup>1</sup> as to a possible analogy of the two excited states to the  $2p$  and  $3p$  states of the Na atom.)

*Analogy between bands of  $N_2^+$  and CN.* The very close resemblance of the  $CO^+$  spectrum to that of BO is probably paralleled by a similar analogy between the spectra of  $N_2^+$  and CN. The “negative nitrogen” bands, which are definitely known to be due to  $N_2^+$ , resemble the violet CN bands extremely closely in structure (including the appearance of the CN type doublets)<sup>14</sup>, in position in the spectrum, and in the relative values of the coefficients of  $n'$  and  $n''$ . Although no second system of  $N_2^+$  bands has been found analogous to the red CN bands, it may well be that these lie in the near infrared so as to have escaped observation. The fact that the negative nitrogen bands have been obtained by Duffendack<sup>15</sup> in the low-voltage arc at a potential just about enough above the ionizing potential to correspond to  $\nu^e$  (3.2 volts), indicates that their final

<sup>14</sup> M. Fassbender, *Zeits. f. Phys.* **30**, 73 (1924).

<sup>15</sup> O. S. Duffendack, *Phys. Rev.* **20**, 665 (1922); *Astrophys. J.* **61**, 221 (1925).

<sup>16</sup> R. S. Mulliken, *Cf Nature*, Dec. 13, 1924.

<sup>17</sup> O. S. Duffendack, and D. C. Duncan, *Phys. Rev.* **23**, 295 (1924).



state must be the normal state of the  $N_2^+$  molecule, again in analogy to the CN bands<sup>16</sup> and the BO bands.<sup>1</sup>

Simultaneously with the negative nitrogen bands, according to Duffendack and Duncan,<sup>17</sup> a new system appears further in the ultraviolet; these Duffendack<sup>15</sup> has called the *second negative bands*. Since  $\nu^e$  here considerably exceeds the value which it has for the first negative bands, according to Duffendack,<sup>15</sup> it seems probable, however, that these bands are not emitted by the  $N_2^+$  molecule but by a neutral molecule in which both of the final pair of electrons (whose analogy to the pair of valence electrons of such a metal as Mg has been suggested above) are excited.

The negative nitrogen bands differ from the other bands of their class in showing a peculiar alternating intensity in each branch which has led Dieke<sup>18</sup> to propose a subdivision of each branch into two. This peculiarity, however, seems to be characteristic of homopolar molecules,<sup>9</sup> and the proposed change, as first pointed out by Birge (private communication), would involve a conflict in the calculated moment of inertia and internuclear distance (cf Table I) with the remarkably consistent and reasonable values obtained by the usual interpretation for all the members of this class of emitters (and for related molecules such as  $N_2$  and CO). Dieke's interpretation would halve the value of  $r_0$  given in the table for  $N_2^+$ .

#### OTHER ONE-VALENCE-ELECTRON BANDS

Of the members of series A and B above, BO and CN, and their analogues  $CO^+$  and  $N_2^+$ , have now been discussed; BeF and MgF are the probable emitters of the known<sup>20</sup> beryllium and magnesium fluoride bands (cf Table I and notes); there remain SiN and AlO. The SiN bands, first described by Jevons<sup>21</sup> and recently studied by the writer,<sup>22</sup> show close analogy to the violet CN bands.<sup>22</sup> From this one might expect in the red or near infrared a system of SiN bands analogous to the red CN bands. Although no such bands have been detected, a new double-headed system ( $\Delta\nu = 27$ ) has been found<sup>22</sup> whose final state may possibly be the same as the initial state of the hypothetical red SiN bands.

*Bands of AlO.* The last member of series A and B is accounted for if the familiar *aluminum bands* centering in the green are attributed to AlO.

<sup>18</sup> G. H. Dieke, *Zeits. f. Phys.* **31**, 326 (1925).

<sup>19</sup> R. Mecke, *Zeits. f. Phys.* **31**, 709 (1925). This characteristic of homopolar molecules was also independently pointed out (private communication) by R. T. Birge.

<sup>20</sup> S. Datta, *Proc. Roy. Soc.* **99A**, 436 (1921 ; **101A**, 187 (1922)).

<sup>21</sup> W. Jevons, *Proc. Roy. Soc.* **89A**, 187 (1913).

<sup>22</sup> R. S. Mulliken, *Nature*, (March 22, 1924) and (July 4, 1925); *Phys. Rev.* **26**, 319 (September 1925).

The question has long been in dispute<sup>23</sup> as to whether these bands are due to the metal or to the oxide. Since the structure of the bands is that of a diatomic emitter, the alternatives are  $\text{Al}_2$  and  $\text{AlO}$ . The isotope effect is unfortunately not available as a criterion, on account of the absence of Al isotopes. The vibration frequencies in the initial and final states<sup>24</sup> (cf Table I) for the bands in question are of the same order of magnitude as for  $\text{SiN}$ , and are more in accord with the undoubtedly tightly-bound  $\text{AlO}$  than with a loosely-bound compound such as  $\text{Al}_2$  whose bands would presumably resemble the  $\text{Na}_2$  bands. Also Mörikofer has shown that the bands are emitted in all parts of the Al arc, indicating that, although easily excited, their emitter is also stable under more violent conditions.<sup>25</sup> Furthermore, the results of an unpublished calculation from measurements on structure lines, made by W. C. Pomeroy and R. T. Birge and kindly rendered available to the writer, give for  $\text{AlO}$  an internuclear distance  $1.615 \times 10^{-8}$  cm, not far from that of  $\text{SiN}$ . The corresponding calculated value  $1.38 \times 10^{-8}$  for  $\text{Al}_2$  seems too small for a loosely-bound molecule composed of two atoms with complete shells and with three additional outer electrons in fairly large orbits. The larger values of  $r_0$  for  $\text{AlO}$  and  $\text{SiN}$  than for  $\text{BO}$  and  $\text{CN}$  are in accord with expectation, on account of the extra electron shell present in the positive ions of the former. Also, the structure of the bands is of the violet  $\text{CN}$  doublet type.

The great affinity of aluminum for oxygen, and the analogy to  $\text{BO}$ , also favor  $\text{AlO}$ . Experiments by the writer show that the bands are obtained in active nitrogen under the same conditions as are required for the  $\text{BO}$  bands.  $\text{AlCl}_3$  vapor was introduced into active nitrogen containing varying amounts of oxygen. With no oxygen, a weak continuous spectrum in the visible resulted. When enough oxygen was added so that the  $\beta$  bands of active nitrogen ( $\text{NO}$  bands) exceeded in intensity the  $\alpha$  bands ( $\text{N}_2$  bands), the bands which are here attributed to  $\text{AlO}$  became faintly visible; the strongest heads were identified both visually and photographically.<sup>26</sup>

#### ANALOGIES IN OTHER SERIES OF BANDS

*Two-valence-electron bands.* If the molecules of series A and B resemble alkali metal atoms, molecules having one more electron, such as  $\text{CO}$ ,  $\text{NO}^+$ ,  $\text{N}_2$ , and  $\text{SiO}$ , should show analogies to the alkaline earth metals,

<sup>23</sup> H. Kayser and H. Konen, *Handbuch der Spektroskopie*, Vol. 7, section on Al.

<sup>24</sup> R. Mecke (*Phys. Zeit.* 26, 235, 1925) gives the equation for the heads.

<sup>25</sup> R. Mörikofer, Dissertation, Basel, 1925.

<sup>26</sup> It cannot be stated positively that the bands were not weakly present (and obscured by continuous background) when the nitrogen was free from oxygen; but there is no evidence for this.

e.g., in degree of multiplicity of electron levels and (cf above under  $N_2^+$  in regard to simultaneous excitation of electrons in  $N_2$ ) in occurrence of double electron jumps. The change from odd to even multiplicity shown

TABLE I  
Constants of emitters of the CN type

Emitter	$\nu^e$	Excited states				Probable normal state			
		$a'$	$b'$	$B_0'$	$r_0(10)^8$	$a''$	$b''$	$B_0''$	$r_0(10)^8$
BeF	{33180-33215	1157	8	....	....	1250	12	....	....
	{Below $\lambda 2200?$	....	....	....	....				
$B^{10}O$	{23522-23648	1248	10.6	1.92	1.20	1873	11.8	2.30	1.09
	{42881	1269	10.0	2.03	1.16				
$CO^+$	{20346-20472?	1550?	14.1?	{1.56 1.28}		2199	15.5	1.97	1.14
	{45637	1701	26	{1.60 1.26}					
CN	{14376-14430	1728	13.5	<1.89>	1.17	2056	13.5	1.89	1.17
	{25800	2244	20.3	1.96	1.13				
$N_2^+$	{Near infra-red?	....	....	....	....	2187	16.1	1.92	1.12
	{25547	2398	26.2	2.07	1.08				
SiN	{Near infra-red?	....	....	....	....	1145	6.6	0.74	1.55
	{24234	1016	17.8	0.73	1.56				
AlO	{Near infra-red?	....	....	....	....	971	7.2	0.64	1.62
	{20646	866	4.0	0.61	1.65				

Notes for Table I. General: the values of  $\nu^e$ ,  $a$ , and  $b$  are for heads, except in the cases of SiN, the violet CN bands, and the high-frequency  $CO^+$  bands, and serve merely to give an approximate idea of the true values, except that in the doublet bands, the heads given are Q heads and should nearly coincide with the true  $\nu^e$  values; also, the values given would be somewhat changed if half-integral vibrational quantum numbers were adopted, as they probably should be.<sup>1,2</sup> The constants for BeF are from an analysis of Datta's results (ref. 20); Datta reported only three heads for each band (at 33218, 33215, and 33180 for the 0,0 band), but it is possible that a weak fourth head (the third head is weak) may have escaped notice among the numerous structure lines; although some data are given on structure lines, and the region of the null-line can apparently be located approximately, reliable values of  $B'$  and  $B''$  could not be obtained. The formulation of the heads requires a relatively large term in  $n'n''$  (about  $-5n'n''$ ), which must be due to variation with  $n'$  and  $n''$  of the (evidently rather large) distance from head to origin;<sup>27</sup> the fact that the mutual separation of the three observed heads is not constant may be ascribed to this fact combined with the existence of appreciable differences in the values of  $B$  for the different heads. For the low-frequency  $CO^+$  bands (comet tail bands) the constants  $\nu^e$ ,  $a$ , and  $b$  are as given by Birge,<sup>13</sup> although the true values may be considerably different, due to uncertainty as to the correct assignment of vibrational quantum numbers; the values of  $\nu^e$ ,  $a$ , and  $b$  for the other  $CO^+$  bands are from Blackburn's published equations;<sup>12</sup> the  $B_0'$  and  $B_0''$  values are preliminary values from unpublished work of Blackburn, and involving a revision of his published values. For CN,  $N_2^+$ , SiN, AlO, respectively, see refs. 24, 14, etc.; 15; 22; 24 and text.

<sup>27</sup> R. S. Mulliken, Phys. Rev. 25, 119-38 (1925).

in passing from the spectrum of  $N_2$  to that of  $N_2^+$  (this change being analogous to that expressed by the alternation law in line spectra) has been discussed by Mecke, who has also discussed the application of the displacement law of line spectra to the emitters of band spectra, in particular to hydrides.<sup>3</sup>

*Three-valence-electron bands.* Further, odd molecules like NO, with one more electron than for the  $N_2$  type, should resemble atoms of the aluminum family; the probable spectra of NO ( $\beta$  and  $\gamma$  bands of active nitrogen, the latter being the same as the third positive nitrogen bands)<sup>1</sup> show electronic doublets (see above), in accord with the expected even multiplicity. Nitric oxide, it may be recalled, is one of the very few substances composed of odd molecules whose chemical activity is sufficiently low to permit its existence in quantity under ordinary conditions.

*No-valence-electron bands.* Again, going backward from series A and B, molecules of the type of LiF (and HF, NaCl, etc.), BeO, BN, containing no unused valence electrons, should have an analogy with the rare gases; this is indeed borne out by the complete absence<sup>2</sup> of electronic band spectra in the case of the halides (and apparently for BN), but is seemingly contradicted in the case of the alkaline earth oxides by the occurrence of characteristic band spectra (but see discussion in a previous paper<sup>2</sup>).

*Note added in proof.* Since the above was written, a part of the relations noted have been pointed out independently by R. T. Birge (Nature, August 8, discussion of the combination bands of  $CO^+$ ) and R. Mecke (Naturwissenschaften, August 7, combination bands of  $CO^+$  and analogies between BO and  $CO^+$ ; CN and  $N_2^+$ ).

JEFFERSON PHYSICAL LABORATORY,  
HARVARD UNIVERSITY,  
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## INDIRECTLY EXCITED FLUORESCENCE SPECTRA

BY S. LORIA\*

## ABSTRACT

Fluorescence spectrum of thallium mixed with Hg vapor.—(1) *Repetition of experiments of Franck and Cario.* The illuminated end of the quartz tube containing Tl metal was placed in the hottest part of the furnace to avoid condensation. In the fluorescence spectrum all Tl lines to be expected theoretically, from  $2p_1-2s$  to  $2p_1-4d_1$  and  $2p_1-5d_2$  were identified. This excitation shows that the life of the  $2p_1$  state is for Tl atoms of the order of  $10^{-8}$  sec. (2) *Enhancing effect of inert gases.* Series of spectrograms with the same tube confirmed the results of Donat. As the pressure of A or N<sub>2</sub> was increased the intensity of  $\lambda\lambda 5350, 3776$  and  $2768$  increased rapidly reaching a maximum for 5 to 20 mm of A or 5 to 10 mm of N<sub>2</sub>. A trace of O<sub>2</sub> neutralizes this enhancing effect. (3) *Experiment with Tl vapor distilling past the window.* In this case a "negative effect" was observed, the addition of a neutral gas decreasing the fluorescence. This was probably due to the interference of the inert gas on the rate of distillation and hence on the amount of Tl present near the window. (4) *Experiments with closed tubes at uniform temperature.* The enhancing effect was also obtained with these tubes, showing that it cannot be an indirect effect of the interference of the neutral gases with the distillation of the Tl vapor in Donat's experiments, but is definitely associated with the presence of the neutral gas. (More intense fluorescence was obtained with N<sub>2</sub> at 5 mm and Hg at 0.16 mm than with N<sub>2</sub> at 8 mm and Hg at 0.5 mm, the Tl being at 0.45 mm.) (5) *Conclusions regarding role of Hg atoms in the  $2p_3$  state.* These results confirm the assumption of Franck and Donat as to the part the Hg atoms in the metastable  $2p_3$  state take in the energy transfer to normal Tl atoms. Comparison of spectrograms at different partial pressures indicates that the metastable Hg atom may survive many collisions with normal A or N<sub>2</sub> molecules but easily gives up its energy when colliding with normal Tl or Hg atoms, probably more easily to Tl than to Hg.

## INTRODUCTION

1. Klein and Rosseland<sup>1</sup> concluded from theoretical considerations, based on the application of the second law of thermodynamics to a system of atoms, electrons, and radiation, that so-called collisions of the second kind must occur between activated atoms and electrons. Due to such a collision an activated atom may return to its normal state without sending out the radiation that is connected normally with this transition, the corresponding quantum  $h\nu$  being then distributed between both colliding particles in the form of kinetic energy, according to the principle of momentum.

\* Professor of Physics at the University, Lwow, Poland.

<sup>1</sup> O. Klein and S. Rosseland, *Zeits. f. Phys.* 4, 46 (1921).



2. J. Franck<sup>2</sup> extended this idea of collision of the second kind to a system which contained besides electrons, activated atoms, and radiation, also normal atoms of a suitably chosen vapor. He then predicted that activated mercury atoms, when colliding with neutral atoms of a vapor which does not absorb the effective radiation and which has its resonance potential below 4.9 volts, may excite the atoms of the vapor, causing them to emit their fluorescence spectra. These spectra ought to contain all lines corresponding to transitions from energy levels  $E_2$  to  $E_1$ , where  $E_2 - E_1 \leq 4.9$  volts. Experimental investigations carried out by Cario,<sup>3</sup> Franck and Cario,<sup>4</sup> Kopfermann,<sup>5</sup> and Donat,<sup>6</sup> confirmed this theoretical prediction in the case of Tl, Cd, Pb, Bi, Ag, and In. On account of the analogy of this excitation of spectral lines with the process of sensitization of photographic plates, Franck called the new phenomenon the "sensitized fluorescence."

3. A closer investigation of the spectra revealed two new facts. (1) Some lines corresponding to energy transfers  $E_2 - E_1 > 4.9$  volts appeared on the plates. (2) Abnormally high intensities of some of the lines could not be accounted for by considerations of the theoretical probability of collisions with the required amount of relative energy. To account for these Franck found it necessary to assume (a) that the excitation energy of an activated Hg atom may be added to the relative kinetic energy of the colliding particles, so that the sum of both exceeds under favorable conditions the equivalent of 4.9 volts; (b) that due to collisions some of the activated Hg atoms ( $2p_2$  state) may be thrown over into the lower metastable state for a time longer than the life-time in the  $2p_2$  state.

4. The correctness of the last assumption seemed strikingly confirmed by some new results obtained by Donat. He found that when A or  $N_2$  is added to the mixture of Hg and Tl showing the sensitized fluorescence of the latter, the intensity of all Tl lines increased remarkably, while the resonance of Hg became weaker. It has been shown that even at atmospheric pressure of A — when, as we know from investigations of Wood,<sup>7</sup> Cario,<sup>8</sup> and Stuart<sup>8</sup> the resonance of Hg vapor is largely reduced — the Tl lines  $\lambda\lambda 5350, 3776, 3529$  and others appear stronger than without A present. This relatively high intensity of the Tl lines in the presence

<sup>2</sup> J. Franck, *Zeits. f. Phys.* 9, 259 (1922).

<sup>3</sup> G. Cario, *Zeits. f. Phys.* 10, 185 (1922).

<sup>4</sup> G. Cario and J. Franck, *Zeits. f. Phys.* 17, 202 (1923).

<sup>5</sup> H. Kopfermann, *Zeits. f. Phys.* 21, 316 (1924).

<sup>6</sup> K. Donat, *Zeits. f. Phys.* 29, 345 (1925).

<sup>7</sup> R. W. Wood, *Phys. Zeits.* 13, 353 (1912).

<sup>8</sup> H. Stuart, *Zeits. f. Phys.* 32, 262 (1925).

of a large number of A atoms, when the probability of a collision of an activated Hg atom with an A atom is enormously greater than the probability of its collision with a Tl atom, makes it necessary to assume that many Hg atoms may be thrown over into a metastable orbit  $2p_3$  and retain their energy for a relatively long time. This explanation involves, however, a new important assumption as to the nature of the metastable  $2p_3$  state of the Hg atoms.

Till now we have defined the metastable state of an atom, according to the requirements of the selection principle, as a state from which the atom cannot come back to the normal state in the ordinary way, i.e., by sending out its surplus energy in the form of radiation. We should expect such an atom to persist in the metastable state indefinitely, provided no collision with another atom and no action of external electric or magnetic fields intervene. Thus, collisions being the only possible mechanism of bringing an atom out of a metastable state, we should expect its time of existence in such a state to be completely determined by its collisions with other atoms. Hence, if we accept Franck's explanation of the increasing effect of A on the sensitized fluorescence of Tl vapor, we have to assume furthermore that the *Hg atoms in  $2p_3$  state may endure very many collisions with A atoms or  $N_2$  molecules without going over to a lower state until they happen to collide with a Tl atom, to which they then transfer immediately the whole amount of potential energy.*

It appeared desirable, on account of the peculiarity of this last assumption, to re-examine the phenomena discovered by Franck, Cario, and Donat, repeating their experiments under better defined conditions of temperature and pressure with the purpose of finding, if possible, some other explanation.

#### I. INDIRECT EXCITATION OF THALLIUM FLUORESCENCE IN MIXTURE WITH MERCURY VAPOR

5. The experimental method used for excitation of the Tl fluorescence through collisions with activated Hg atoms was quite similar to that used by Franck and Cario.

A Cooper-Hewitt vertical mercury arc, mounted between the poles of a small electromagnet and cooled down by a strong blast of air, was used as source of illumination. A quartz lens (4 cm diameter, 7.5 cm focus) concentrated the unresolved beam of light on a flat window of a quartz tube, illuminating it from the side at about  $45^\circ$ . The tube was in a horizontal position, its shape and dimensions being as shown in Fig. 1 (tube A).<sup>9</sup> Within it was placed, in the position indicated by the black

<sup>9</sup> At first 2 mm thick plane polished quartz plates were fused on the end of the tube. It has been found, however, that such windows when heated above  $300^\circ\text{C}$ , are very



spot, a piece of carefully purified metallic Tl, the whole being then inserted in an electrically heated furnace with two fused quartz windows as shown. The furnace was built in such a way that the illuminated part of the tube could be kept at a temperature a little higher than the rest, in order to prevent the flat end of the tube from being covered with a thin layer of condensed metal.

The rear end of the quartz tube was connected with a diffusion pump and contained a few cc of pure mercury in a vertical side tube which was heated by another furnace. Provisions were made to keep the part of the tube between the two furnaces at a temperature higher than that of the mercury.

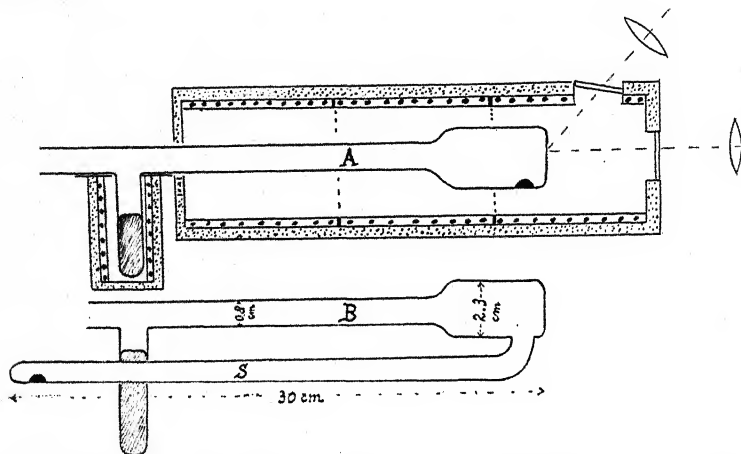


Fig. 1. Diagram of apparatus showing tube *A* used for repeating experiment of Franck and Cario and of Donat, also tube *B* in which the liquid Tl is 30 cm from the window.

A second quartz lens enabled the image of the illuminated window to be thrown upon the slit of a large Hilger spectrograph. Cramer's isochromatic plates (very sensitive in the region of the green Tl lines) gave the most satisfactory results.

6. The first trace of  $\lambda 5350$  could be detected visually in the spectrum when the temperature of the main furnace was about  $500^{\circ}\text{C}$  and the temperature of Hg higher than  $60^{\circ}\text{C}$ . Photographs obtained after one hour exposure with Tl at  $800^{\circ}\text{C}$  and Hg at  $100^{\circ}\text{C}$  show almost all the

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easily attacked by the vapors. They may be cleaned in an oxygen-hydrogen flame, but even then they do not last long and must be too often renewed. Far more satisfactory results could be obtained by simply blowing one end of a sealed-off tube flat. Windows of that kind can be made sufficiently even and plane, and endure many hours of exposure without showing any loss of transparency.

lines that could be expected according to Bohr's energy level scheme. The following lines were identified.

5350	$2p_1-2s$	2918	$2p_1-4d_1$
3776	$2p_2-2s$	2826	$2p_1-4s$
3529	$2p_1-3d_2$	2768	$2p_2-3d_2$
3519	$2p_1-3d_1$	2711	$2p_1-5d_2$
3230	$2p_1-3s$	2580	$2p_2-3s$
2922	$2p_1-4d_2$	2380	$2p_2-4d_2$

The existence of the lines 2711 ( $2p_1-5d_2$ ), 2918 ( $2p_1-4d_1$ ), 2922 ( $2p_1-4d_2$ ) is very significant. It shows that in some Tl atoms electrons have been raised up to  $4d_1$ ,  $4d_2$ ,  $5d_2$  levels. Energy equivalent to 4.9 volts is not sufficient to bring them to these levels from the normal  $2p_2$  orbit. The energy transfer from Hg atoms must have occurred while the electrons were in  $2p_1$  state, brought there by collisions with normal atoms, or more likely on their way back from higher states. The possibility of excitation of lines corresponding to such high energy levels like  $4d_1$ ,  $4d_2$ , and  $5d_2$  shows at any rate that the lifetime of the  $2p_1$  state is for Tl atoms at least of the same order of magnitude as the time between collisions of Tl and Hg under our conditions, i.e., about  $10^{-6}$  sec.<sup>10</sup>

## II. THE EFFECT OF A AND N<sub>2</sub> ON THE INDIRECT EXCITATION OF Tl-FLUORESCENCE

7. The experimental arrangement remained the same as before, only provisions were made for introducing gases under known pressure.

Argon supplied by the General Electric Company was guaranteed to be 99.8 percent pure, the main impurity being nitrogen. Nitrogen made from air by the ordinary process (ammonium chloride, ammonium hydroxide, and copper) had been passed through a liquid air trap and a tube with hot copper gauze.

The effect of A under different pressures up to 1 atm. is clearly shown in Fig. 2. The first spectrum shows the Franck-Cario effect in Tl without argon. All six following spectra show the Tl lines enhanced by A at

<sup>10</sup> This time may be computed from the well-known equation (L. Boltzmann, Vorlesungen über Gastheorie) for the number of collisions

$$\nu = \sigma^2 p \times 2666 \cdot 6 \sqrt{(2\pi N/k\theta)} (m+m_1)/mm_1$$

where  $\sigma$  = the mean value of the diameters of Tl and Hg;  $p$  = the total pressure;  $N = 0.607 \times 10^{24}$ ;  $k$  = Boltzmann's constant  $1.37 \times 10^{-16}$ ;  $\theta$  = the temperature, 1073°K;  $m$  = the atomic weight of mercury, 200.6;  $m_1$  = the atomic weight of thallium, 204. If we take the diameter of Hg in the normal state, i.e.,  $3.5 \cdot 10^{-8}$  cm and the diameter of Tl obtained from the x-ray analysis of crystals,  $3.4 \cdot 10^{-8}$  cm we get  $T = 1/\nu = 2 \times 10^{-6}$  sec. Assuming that all mercury atoms are activated and have then according to Stuart (H. Stuart, Zeits. f. Phys. 32, 267, 1925) the diameter  $3.4(3.5 \times 10^{-8}$  cm), we get  $T = 1/\nu = 5.5 \times 10^{-6}$  sec.

different pressures. This remarkable enhancement of all Tl lines is in agreement with Donat's statement. However, the effect he obtained was different for different lines; some of them showing more or less pronounced maxima at pressures between 1 and 100 mm Hg, whereas no maxima were noticed by him for the lines 5350, 3776, 2768; he reports that their intensities increased rapidly with the pressure to a few centimeters and

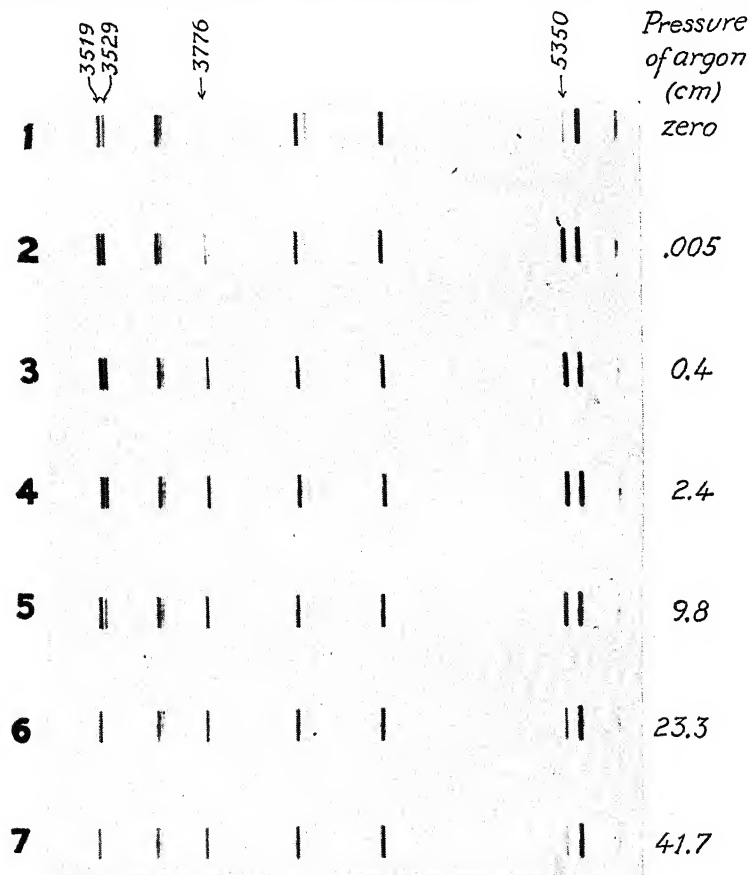


Fig. 2. Spectrograms of fluorescence in mixtures of Tl and Hg vapors, with an inert gas argon also present at various pressures as indicated. The time of exposure in each case was 32 min; the Tl was at 680°C, the Hg at 100°C.

then remained constant up to atmospheric pressure. The results of the present investigation show that a maximum in the effect of A on the intensity of the Tl spectrum appears *on all the lines without exception, but at different pressures*. As may be seen in Fig. 2, the lines 5350, 3776, and 2768 decrease in intensity when the pressure exceeds 2 cm, the optimum being for 5350 between 5 and 20 mm.

The decrease of intensity is naturally explained by the fact that at higher pressures collisions of the second kind must occur as well between argon and excited Tl atoms as between argon and mercury atoms. The maximum is very flat and may not show up as distinctly on photographs taken with longer exposures. This might account for the apparent equal intensity of blackening on Donat's plates.

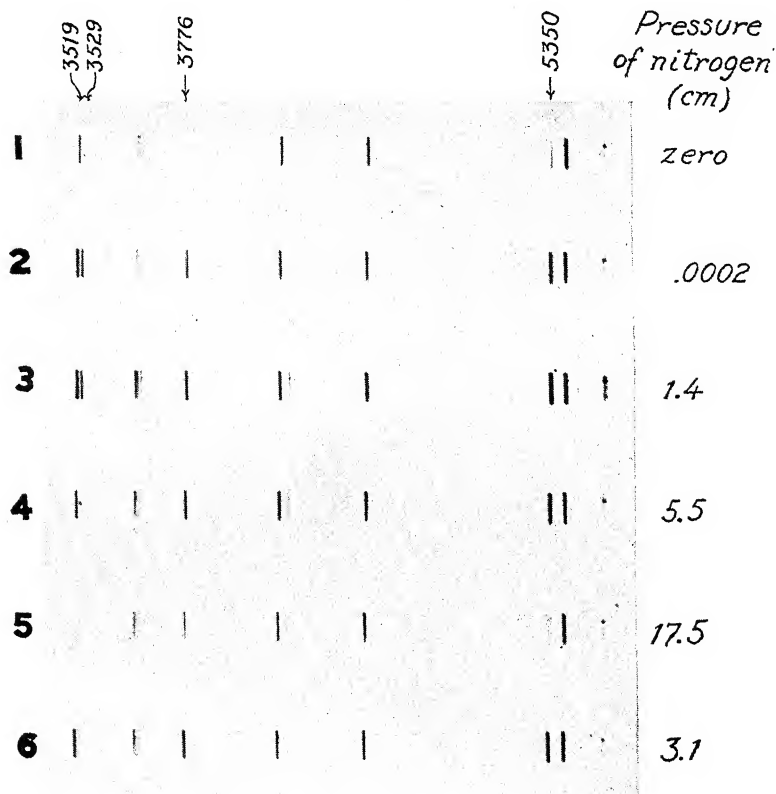


Fig. 3. Fluorescence spectra of Tl and Hg with  $N_2$  present. Exposure 32 min.  
Tl at  $640^\circ C$ , Hg at  $100^\circ C$ .

8. Donat found that pure nitrogen influences the Tl spectrum in the same way as A, the effect being, however, much weaker. A careful investigation of this effect at *very low pressures* shows, however, that the effect of  $N_2$  may be even much stronger than that of A, provided the optimum pressure of the gas is used. *It is enough to introduce into the tube a small fraction of a millimeter of carefully purified  $N_2$  (about  $2 \times 10^{-3}$  mm) to make the whole window shine with vivid, very bright soft green light.* The phenomenon is especially interesting when observed through a

spectroscope. The line 5350 flashes out suddenly and, although it had been much weaker than 5461 of Hg, becomes now many times stronger. The sharp maximum may be clearly seen in Fig. 3. Visual observations have shown that the optimum pressure of  $N_2$  is between 5 and 10 mm. It has been noticed also that when nitrogen at this pressure is brought into the tube the intensity of 5461 of Hg increases remarkably. This

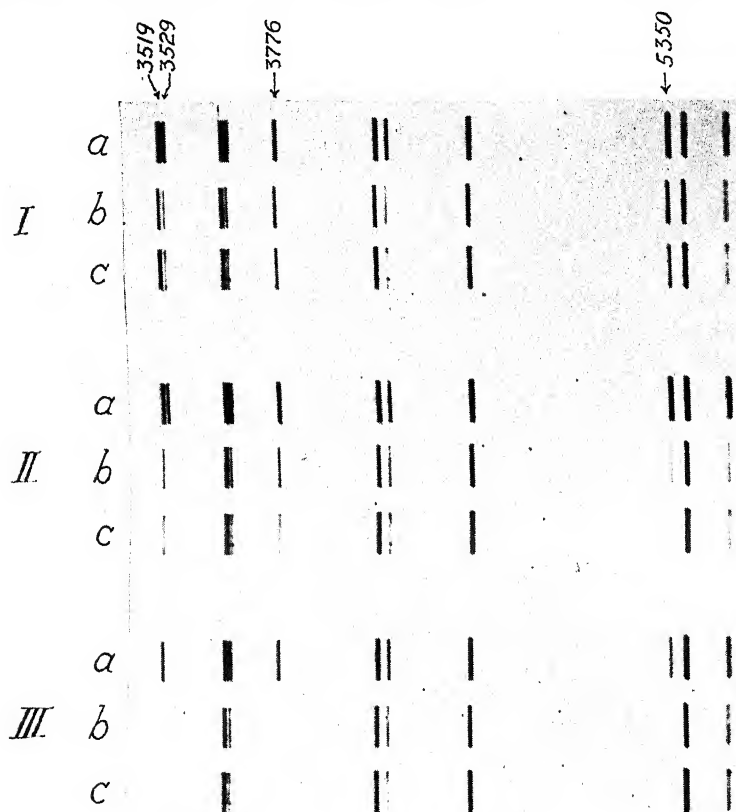


Fig. 4. Fluorescence spectra of sealed off tubes *a*, *b* and *c*.  
The temperature was 680°C for group I, 590°C for group II and 490°C for group III.  
Tube *a*: Tl saturated; Hg at pressure <0.16 mm;  $N_2$  at 5 mm.  
Tube *b*: Tl saturated; Hg at 0.5 mm;  $N_2$  at 8 mm.  
Tube *c*: Tl saturated; Hg at 0.5 mm; no inert gas.

observation is in close agreement with the results obtained by Wood in his investigation of the changes in the intensity distribution of the Hg spectrum due to the presence of nitrogen.<sup>11</sup> The effects of  $N_2$  and A

<sup>11</sup> R. W. Wood, Proc. Roy. Soc. 106, 689 (1924).

on the Tl fluorescence seem to be very sensitive to small traces of impurities, *the most destructive being oxygen*.<sup>12</sup> Nitrogen made from air in the way described above, but not passed over hot copper, extinguished the green Tl line entirely. Also, argon containing a minute amount of air as impurity, weakened the Tl fluorescence remarkably.

9. So far the results of the present investigation are in general agreement with what has been found by Donat.

However, the explanation suggested by him as to the accumulation of energy in the metastable  $2p_3$  state of mercury atoms is, nevertheless, open to serious objections. The conditions under which the new phenomenon has been observed, are not at all defined. One part of the tube A, Fig. 1, containing Tl is kept at 800°C, the other with mercury being at 100°C. The saturation pressure of Tl at 800°C is about 2 mm,<sup>13</sup> the saturation pressure of Hg is 0.3 mm.<sup>13</sup> The fluorescence is a surface phenomenon, the whole process of excitation taking place on the illuminated window.

As long as no gas is present in the tube, the thallium vapor diffuses rapidly away towards the colder part of the tube. Its pressure changes from 2 down to 0.02 mm. Moreover, due to the steep gradient of temperature (from 800°C to 100°C in a distance of 30 cm) the stream of Tl vapor condenses on the way and may pump out mercury from the front part of the tube, decreasing its density below 0.3 mm. These processes evidently tend to decrease the intensity of the fluorescence.

These conditions are totally changed when gas is introduced into the tube. The gas brings in fresh mercury vapor, it slows down the diffusion of Tl vapor and it prevents the mercury from being pumped out by the condensing Tl. These changes tend to increase the intensity of Tl fluorescence. It seems, therefore, not improbable that the effect observed might be partially or even totally explained in the foregoing simple way.

Very instructive in this respect were the results obtained in experiments made with the tube B shown on Fig. 1. Metallic Tl placed at a distance of 30 cm from the window was heated by a special furnace and allowed to diffuse along the whole tube, the stream of vapor being carried through the illuminated portion. The green line of Tl  $\lambda 5350$  appeared at about 700°C. Nitrogen of 5 mm pressure *extinguished* the fluorescence instantaneously; the line *appeared again* in the absence of N<sub>2</sub>. Analogous experiments with A gave similar results. Increase of

<sup>12</sup> H. Stuart found that oxygen is most effective in extinguishing the resonance radiation of mercury.

<sup>13</sup> Landolt-Börnstein, Tabellen.



pressure from 3.5 up to 52 mm caused an increasing *decay* of fluorescence, while the spectrum *brightened up remarkably as soon as the gas was removed*. This "negative" effect could be obtained over and over again with *gases of the same purity* as those which gave "positive" effects in the simpler tube. It has been noticed, however, that the "negative" effect became less pronounced with time, especially after the tube *was allowed to cool down frequently*. Evidently, the metallic thallium distilled slowly over into the main part of the tube bringing it automatically to the same conditions that existed in tubes used before; and, in fact, when the metal was then transferred in vacuum into the main part of the tube, and the side-tube *s* was sealed off, only the regular "positive" effect appeared again. It is evident, therefore, that as long as we work with "open," not uniformly heated tubes, we actually know nothing about the pressures of the components of the metallic mixture. All assumptions as to the nature of the elementary mechanism of energy transfer with or without the co-operation of atoms in the metastable  $2p_3$  state will then necessarily retain a considerable degree of uncertainty.

10. Preliminary experiments had shown that it is not difficult to obtain the sensitized fluorescence of Tl in a *closed tube, heated uniformly* in a furnace. This discovery opened the possibility of a comparison of the intensity of Tl fluorescence in two sealed-off and uniformly heated tubes, one of them containing merely Tl and Hg, the other the same metals in an atmosphere of the gas under known pressure. The pressure of Tl vapor being then determined by the temperature of the furnace, it was only necessary to introduce into the tube a known amount of mercury vapor. It must be emphasized, however, that, according to what has been said before about the processes going on in an "open" tube, while the enhanced fluorescence appears, the pressure of mercury vapor cannot be regarded as known. It was, therefore, necessary to seal off *three* tubes prepared as follows:

The tube *a* connected with the pump and the gas container in the same way as before, was heated up to  $680^{\circ}\text{C}$ , the temperature of the side-tube with mercury being kept at  $90^{\circ}\text{C}$ . Pure  $\text{N}_2$  of 5 mm pressure was then introduced into the tube. *While a very strong effect appeared on the green line 5350, the tube was sealed off from the pumps.*

The tubes *b* and *c* were at first connected together and to the pump and put side by side into the furnace. By shifting the illuminating lens a little one could observe the Franck-Cario effect alternatively in each of them in the same way as before. Under the influence of  $\text{N}_2$  at 8 mm pressure the green fluorescence appeared exceedingly strong. *The tubes were then allowed to cool down to a temperature of  $130^{\circ}\text{C}$ , and were kept at*



this temperature for two hours, the temperature of the mercury being only  $110^{\circ}\text{C}$ . After two hours one of the tubes *b* was sealed off. The other tube *c* was then pumped out and kept under highest vacuum at  $130^{\circ}\text{C}$  for another two hours and then sealed off from the pumps. The temperature of mercury was all the time kept constant at about  $110^{\circ}\text{C}$ .

Each tube was then examined in a uniformly heated furnace. Visual observations made on the green line  $\lambda 5350$  gave the following results.

*Tube a* containing Tl vapor at saturation pressure,  $\text{N}_2$  at 5 mm, mercury vapor at the pressure  $\leq 0.16$  mm. The Tl line appears at the temperature of  $360^{\circ}\text{C}$ , increases rapidly in intensity with increasing density of the vapor and is at  $700^{\circ}\text{C}$  much stronger than 5461 (always present due to reflection and scattering). There is no difference whatever between the appearance and intensity of the spectrum in this sealed-off tube and the phenomenon observed before in an "open" tube under the same conditions.

*Tube b* containing Tl at saturation pressure,  $\text{N}_2$  at 8 mm, and Hg at 0.5 mm. The line appears at about  $410^{\circ}\text{C}$ , increases in intensity with increasing density of the vapor, but does not reach the same brightness at  $700^{\circ}\text{C}$  as in the tube (*a*).

*Tube c* containing Tl at saturation pressure, Hg at 0.5 mm, and no gas. The line does not appear until about  $510^{\circ}\text{C}$  is reached, is remarkably weaker than in *a* and noticeably weaker than in *b*. The appearance and intensity of the spectrum are the same as in open tubes, without gas.

11. Fig. 4 shows the lines 5350, 3776, 3529, 3519, in all three tubes at different temperatures. The comparison of the intensities of the spectra excited in the tubes *a* and *c* shows conclusively that (1) the effect of  $\text{N}_2$  on the intensity of sensitized fluorescence of Tl *persists in uniformly heated sealed-off tubes*; (2) it cannot be explained as due to differences in pressure of Tl or Hg, caused by diffusion and condensation in a not uniformly heated "open" tube.

The comparison of the phenomenon in tubes *b* and *c* shows that the effect is due *entirely to the presence of the gas*, thus confirming Franck's hypothesis as to the part the metastable  $2p_3$  atoms must take in the elementary act of energy transfer.

Finally, comparing the intensities of the spectra excited in the tubes *a* and *b*, we see that the phenomenon observed for the first time by Donat is very strong when the pressure of mercury vapor is lower (0.16 mm) than that of Tl (0.45 mm), and less pronounced when the pressures of mercury (0.5 mm) and Tl are nearly equal. This seems to indicate that the metastable  $2p_3$  atoms *while enduring very many collisions with  $\text{N}_2$  molecules or A atoms may not as easily retain their energy in a collision*

*with normal mercury atoms.* It is, however, possible that the probability of an energy transfer from  $2p_3$  atoms to normal mercury atoms is yet much smaller than the probability of a transfer from  $2p_3$  atoms to Tl atoms. This is indicated by the fact that the enhancing effect of  $N_2$  could be observed accidentally in a tube containing a minute amount of Tl as impurity.

An attempt has been made to excite the sensitized fluorescence of Ga, but no Ga lines could be detected on the plates after one hour exposure at  $960^\circ\text{C}$ . The saturation pressure of Ga being still very low at this temperature it was expected that the presence of  $N_2$  might perhaps sufficiently enlarge the amount of energy available for excitation. The plate obtained after one hour exposure at a temperature of about  $960^\circ\text{C}$  with 5 mm  $N_2$  present in the tube did not show any Ga lines, but very weak traces of  $\lambda\lambda 5350, 3776, 3529, 3519$  of Tl appeared distinctly. The tube had been used previously for experiments with Tl and although cleaned very thoroughly before Ga was put in evidently still contained enough thallium as impurity. It must be emphasized that the Tl lines were just detectable *only when* nitrogen was present, and were not to be found in the spectrum obtained with the same tube without gas.

This observation is valuable for two reasons: (1) It confirms the results previously obtained under conditions that exclude the possibility of the effect investigated being due to diffusion or condensation processes. (2) It indicates that the probability of an energy transfer through collisions from  $2p_3$  atoms to Tl atoms is very much larger than the probability of such a transfer from  $2p_3$  to normal Hg atoms.

The writer wishes to express his best thanks to Professor R. A. Millikan for the opportunity of carrying out experimental research in the Norman Bridge Laboratory, and for his stimulating interest throughout this investigation. He is also indebted to Dr. I. S. Bowen for his valuable assistance in the photographic part of the work.

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PASADENA, CALIFORNIA  
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## SCATTERING OF ELECTRONS IN IONIZED GASES

BY IRVING LANGMUIR

## ABSTRACT

Velocity distribution of electrons in low pressure discharges from hot cathodes.—Analysis of the current received by a collector placed opposite a hot cathode indicates that there are three groups of electrons present; (1) *primary electrons* which retain practically all the momentum they acquired in passing through the positive ion sheath around the cathode; (2) *secondary electrons* moving in random directions with a Maxwellian velocity distribution corresponding to a temperature roughly proportional to the energy of the primaries (200,000° for 100 volt primaries) and approximately independent of the nature or pressure of the gas or the current density; (3) *ultimate electrons* having a Maxwellian distribution of velocities corresponding to a much lower temperature than that of the secondaries, a temperature which is independent of the current density or the voltage of the primary electrons and which varies with the gas used and decreases slowly as the pressure is raised. The number of ultimate electrons is roughly 1000 times that of the primaries and secondaries for mercury vapor, although relatively less numerous in the case of hydrogen. In the uniform positive column of arcs only ultimate electrons are present.

The velocity distribution of the primary electrons may be resolved into a drift velocity normal to the cathode surface and a random motion with a Maxwellian distribution corresponding to a temperature which varies approximately with the square of the current and is a maximum at a mercury vapor pressure of about 0.6 bar, falling to a low value at 8 bars, and is considerably higher with 35 volts accelerating potential than with 80 volts. Under favorable conditions with 40 mil-amp. this temperature may rise to 80000° and there are then appreciable numbers of these primaries which can reach a collector charged to a potential as much as 40 volts below that of the cathode. Experiments with two crossed electron beams prove that the secondary and ultimate electrons, directly or indirectly, are responsible for very little if any of the scattering.

A study of the ultimate electrons in the positive column of a low voltage mercury arc shows that the Maxwellian velocity distribution corresponding to a high temperature (30000°) is maintained in a small tube in spite of the fact that the negatively charged walls of the tube constantly tend to disturb this distribution by selective removal of the faster electrons. The number of collisions of the electrons with each other and with atoms were far too few to maintain the observed distribution. Measurements of the mobilities of electrons in arcs and of the electron concentration differences produced by a transverse magnetic field gave values for the mean free path only 1/10 as great as the values determined by a direct method. These results all indicate that the electrons in low pressure arcs suffer many changes of momentum during the time intervals between successive collisions between atoms, ions or electrons.

*Mechanism of electron scattering.*—After analyzing the effects to be expected when a beam of primary electrons encounters a cloud of stationary electrons or a cloud of particles of small mass but of high temperature, it appears that the experimental results for the ratio of the scattering to the average retardation of

the beam was best accounted for by collisions with a cloud of radiation quanta, a kind of Compton effect. The observed scattering is, however, about  $10^{16}$  times greater than a normal Compton effect would give. It is suggested that the joint action of excited atoms and radiation may multiply the Compton effect sufficiently, or it may be that the presence of a free electron within a distance of a wave-length from an excited atom may greatly increase the probability of a quantum jump and that momentum is delivered to the electron in the process. In arcs the ultimate electrons may be in a kind of thermal equilibrium with radiation and excited atoms.

*Scattered electrons in high vacuum.*—In connection with a study of the Barkhausen-Kurz effect and in a magnetron with negatively charged end plates, evidence of the presence of electrons with abnormally high speeds has also been obtained. These have been explained as due to electric oscillations, but the effects have also been obtained when oscillations are not present. This seems to indicate that electron scattering similar to that observed in low pressure gases can also occur in high vacuum.

### I. ELECTRONS IN THE POSITIVE COLUMN OF LOW VOLTAGE ARCS

*Distribution of velocities.* By studying the volt-ampere characteristics of small electrodes or collectors placed in the path of an arc in mercury vapor at low pressures, it has been found<sup>1,2</sup> that the free electrons in the arc are moving in nearly random directions with velocities which are distributed quite accurately in accordance with Maxwell's distribution law.

When the collector is at large negative potentials with respect to the surrounding gas, it receives only positive ions, but at higher potentials (algebraically) electrons also are collected. At first only electrons of the highest velocities are able to reach the collector against the retarding potential, but as the potential is raised, making the retarding field weaker, electrons of lower velocity can be collected. If the velocities of the electrons are distributed according to Maxwell's law, the logarithm of the electron current flowing to a negatively charged collector should be a linear function of the potential of the collector, with a slope (when plotted using natural logarithms) of  $e/kT$ , where  $T$  is the temperature corresponding to the electron velocities and  $e/k$  has the value 11600 degrees per volt.

When the collector is made positive with respect to the surrounding gas the electron current increases with the potential more slowly and according to entirely different laws. Thus the semi-logarithmic plot of the current-voltage characteristic should be a straight line only for negative voltages and a kink therefore should occur in the curve at a point at which the potential of the collector is the same as that of the

<sup>1</sup> Langmuir, Jour. Frank. Inst. 196, 751 (1923).

<sup>2</sup> Langmuir and Mott-Smith, Gen. Elec. Review 27, 449, 538, 616, 762, 810 (1924).

surrounding gas. By this method collectors may be used to measure the true space potentials.

When a small plane collector is at the space potential in an arc in mercury vapor, the electron current is about 400 times as great as the positive ion current which flows when large negative voltages, sufficient to repel all electrons, are used. Thus, if the collector is disconnected (or is allowed to "float") it charges itself negatively with respect to the surrounding gas until it is able to repel  $399/400^{\text{th}}$  of all the electrons which move towards it, the electrons and positive ions then being collected in equal numbers. Experiments with mercury vapor, hydrogen, nitrogen, argon and neon at low pressures have shown that the semi-logarithmic plots for negative voltages are usually surprisingly straight over very wide ranges of current. The straight semi-logarithmic plot of the electron current extends to negative voltages far beyond that to which the collector charges itself when it is floating. For example, the straight plot was easily observed down to currents only  $1/6000^{\text{th}}$  of the total current.<sup>3</sup> A. F. Dittmer working with Karl Compton at Princeton has recently found, using an improved method by which positive ions and electrons are separated, that with a 40 milli-ampere arc in nitrogen at 8 bars pressure, the straight line plot extends down to current densities of less than  $10^{-5}$  of the total current density. The electron temperature in this case was about  $50000^{\circ}$ .

*The electron temperatures* corresponding to these straight plots are practically independent of the current densities in the arcs, but increase as the pressure is lowered. For example, currents of from 0.1 to 5 amperes in a tube 3 cm in diameter gave electron temperatures of about  $30000^{\circ}$  with mercury vapor at 1 bar;  $20000^{\circ}$  at 5 bars, and  $10000^{\circ}$  at 30 bars. With other gases the electron temperatures are usually higher.

If thermal equilibrium existed in the ionized gas the electrons would of course have a Maxwellian distribution of velocities corresponding to the temperature of the gas. If this distribution is disturbed by any external cause it tends to re-establish itself through the agency of every mechanism by which electron velocities can be modified. For example, collisions of electrons with each other, with atoms or excited atoms, or the interaction of electrons with the black body radiation, will all tend to bring back the Maxwellian distribution of the electrons. The rate of re-establishment of this distribution would be different for each mechanism if that alone were allowed to act. Corresponding to each mechanism we may therefore conceive of a "time of relaxation" which is the time

<sup>3</sup> See, for example, Fig. 1 in Gen. Electric Rev. article (loc. cit.<sup>2</sup>), p. 451.



that would be needed for any disturbance in the Maxwellian distribution to fall to  $1/e^{\text{th}}$  of its value, if only the one mechanism were effective.

We will consider first the interaction between atoms and electrons. The mercury atoms which strike the walls of the tube deliver their surplus energy and leave the glass with a kinetic energy corresponding to room temperature. For mercury vapor at 1 bar and a temperature of  $300^{\circ}\text{K}$ , there are  $2.4 \times 10^{13}$  atoms per  $\text{cm}^3$ . Measurements with collectors in a 2 amp. arc in a 3 cm tube have shown that there are  $8 \times 10^{10}$  free electrons per  $\text{cm}^3$ . In this case the average distance an atom will travel before colliding with an electron is 1.5 cm and in a tube 3 cm in diameter it will make only about four collisions with electrons between consecutive collisions with the wall. Taking the temperature of the electrons as  $30,000^{\circ}$ , the mercury atom gains on the average only  $0.08^{\circ}$  at each collision. Thus the temperature of the mercury vapor which strikes the walls will be only  $0.3^{\circ}$  above the temperature of the walls. This at least represents the temperature that can be acquired by direct interaction with the electrons. Of course there will be a minute fraction of mercury atoms which collide with excited mercury atoms and thus acquire very high kinetic energy, but we may ignore these at present. The time of relaxation corresponding to the interaction between electrons and atoms by collisions is thus at least 100,000 times too great to be effective in bringing about temperature equilibrium and thus affording a means of maintaining a Maxwellian distribution for the electrons.

Since the normal free path  $\lambda_e$  of electrons under the conditions considered, is 30 cm, it is clear that the average distance an electron would have to travel before colliding with an excited atom would be much greater than this and therefore collisions of the second kind, in the ordinary meaning of this term, cannot be responsible for bringing about the electron velocity distribution. The same may be said of collisions of electrons with each other. The concentration of electrons is only  $1/300^{\text{th}}$  that of the atoms and if we assume the target area of an electron is the same as that of an atom, the average distance that an electron would move before colliding with another electron would be 6400 cm (allowing for the velocity of the electron being struck). A careful calculation has been made, based on Coulomb's law, of the effect of the electric force between the electrons in increasing the transfer of momentum by collisions. It is found that the effective free path varies with the electron velocity, but that the free path is still so great that this kind of interaction between electrons must be completely rejected as a possible mechanism for bringing about the observed Maxwellian distribution.

*Effect of the charged glass walls.* The glass walls of the discharge tube are negatively charged because of the fact that the electron current density in the discharge is greater than the positive ion current density. In accordance with observation we may take the electron current in mercury vapor to be 400 times the ion current. If the electron temperature is  $30,000^\circ$  it can then be calculated (in agreement with experiment) that the walls will be charged to  $-15.5$  volts with respect to the ionized gas and will thus be covered by a positive ion sheath. All electrons which have energy components normal to the surface of the glass of less than  $15.5$  volts will be specularly reflected from the walls without loss of energy, but electrons having energy components greater than this will pass through the sheath and be taken up by the walls except for the few that are reflected back. Thus the walls are continually disturbing the Maxwellian distribution by removing the high speed electrons. We should therefore expect distinct departures from a straight line semi-logarithmic plot at collector voltages below that to which the glass walls become charged, unless there is a mechanism which effectively re-establishes the Maxwellian distribution within a distance less than that which separates the collector from the opposing glass walls.

In the experiments made by Harold Mott-Smith Jr. and the writer with mercury arcs in a tube 3 cm in diameter,<sup>4</sup> the collector which was designated *H* consisted of a square nickel plate 1.9 cm on a side which had been bent into a cylindrical surface which conformed to the inner surface of the tube. If electrons traverse the tube in straight paths with constant velocity and are specularly reflected from the cylindrical walls, the radial velocity components in successive collisions with the walls remain constant. If then the walls of the tube are negatively charged to say  $-15.5$  volts *few electrons can reach a cylindrical collector such as H, with radial components greater than 15.5 volts unless these electrons have acquired this large radial velocity within the distance they have travelled since their last collision with the wall.*

The experiments showed in all cases that the straight semi-logarithmic plot extended to negative voltages far below those to which the collector *H* charged itself when it was allowed to float. This must be taken as proof that the higher velocity electrons were produced from low velocity electrons while these travelled a distance of less than 3 cm.

From the complete absence of a kink in the semi-logarithmic plot at the wall potential we must conclude that the time of relaxation corresponding to the mechanism by which the electrons acquire their Max-

<sup>4</sup> Loc. cit<sup>2</sup>, p. 538.



wellian distribution is small compared to the time taken for the electrons to traverse the tube, in other words, that the free path of the electrons corresponding to this mechanism is small compared to 3 cm.

*Effect of charged conducting walls.* Recently Mott-Smith has carried out experiments with a mercury arc at low pressures passing through a metallic cylinder split lengthwise into two halves, which are insulated from one another. One half was used as a collector while the other was maintained at a series of different negative voltages to see if the velocity distribution of the electrons reaching one electrode was modified in any way as different groups of electrons were removed by means of the opposite electrode. It was found in fact that by charging one electrode so strongly negative that even the high speed electrons were reflected from it, the temperature of the electrons collected by the opposite half-cylinder was distinctly higher than if the electrode were at only  $-15$  volts with respect to the gas so that all the higher speed electrons were removed. *But in both cases a perfectly straight semi-logarithmic plot was obtained.* The removal of the high speed electrons lowered the temperature, but the Maxwellian distribution was established while the electrons moved between the two collectors. Experiments are now in progress by A.F. Dittmer using plane collectors whose distance apart can be varied, to determine directly the rate at which the Maxwellian distribution is brought about.

*Evidence as to the mean free path of electrons.*<sup>5</sup> If a small potential gradient  $dV/dx$  is allowed to act on electrons having a Maxwellian velocity distribution, the electrons drift in the field with an average velocity  $v_z$  given by the mobility equation

$$v_z = 4\gamma\lambda/\pi v \quad (1)$$

where  $\gamma$  the acceleration of the electrons is

$$\gamma = \frac{e}{m} \frac{dV}{dx}, \quad (2)$$

$\lambda$  is the mean free path of the electrons and  $v$  is the average velocity of the electrons (assumed to follow Maxwell's law). Expressing  $v$  in terms of  $T_e$  and inserting the value of  $e/m$  we get

$$v_z = 3.62 \times 10^9 \cdot \frac{\lambda}{\sqrt{T_e}} \frac{dV}{dx} \quad (3)$$

where  $v_z$ ,  $\lambda$  and  $x$  are expressed in cm-second units and  $V$  is in volts.

<sup>5</sup> A brief note on the abnormally small values of the free paths of electrons obtained from the mobility and from the effects of transverse magnetic fields was given in the last paper by Langmuir and Mott-Smith, loc. cit.<sup>2</sup>, p. 819.

The current density  $I_x$  of the arc is related to  $v_x$  by the equation

$$I_x = n_e e v_x$$

or if  $I_x$  is in amp. per  $\text{cm}^2$

$$I_x = 1.59 \times 10^{-19} n_e v_x. \quad (4)$$

Combining these equations

$$I_x = 5.76 \times 10^{-10} \frac{n_e \lambda}{\sqrt{T_e}} \frac{dV}{dx}. \quad (5)$$

With the 2 ampere arc in mercury vapor at 1 bar in a tube 3.2 cm in diameter the current density  $I_x$  was 0.25 amp. per  $\text{cm}^2$ ,  $n_e = 8 \times 10^{10}$ ,  $dV/dx = 0.25$  volts per cm, and  $T_e = 30,000^\circ$ . Substituting these into Eq. (5) and solving for  $\lambda$  we find that the free path  $\lambda$  of the electrons in the arc is 3.8 cm. Direct measurement of the number of 50 to 250 volt electrons which pass through ionized mercury vapor at 1 bar without collision with atoms, give a free path of at least 30 cm. The recent investigations of Ramsauer and others, show that for lower velocities (below those necessary to produce ionization), the free paths tend to increase. A large number of measurements of  $\lambda$  with arcs in mercury vapor at various pressures, in tubes of various diameters and with a wide range of current densities have been made in this laboratory. The free path calculated from the mobility always comes out to be 5 to 10 times lower than can be reconciled with direct determination or with values calculated by the usual methods of the kinetic theory.

The application of transverse magnetic fields of 50 to 100 gauss to a mercury arc at low pressures causes the arc to be deflected to one side. By measuring the *ratio of the electron concentrations* at two points along a diameter of the tube which is perpendicular to the magnetic field, it is possible to calculate the free path by a method entirely independent of that involving the mobility. This method also gives free paths about 10 times smaller than the distances which electrons travel before colliding with atoms as obtained by direct measurement.

Both of these results as well as the rapid establishment of the Maxwellian distribution of electron velocities, suggest that *the electrons in a mercury arc suffer many changes in momentum during the time that elapses between consecutive collisions with atoms.*

*Summary.* This discussion of the results obtained from a study of low pressure arcs shows (1) that the free electrons have velocities with a Maxwell distribution corresponding (in the case of mercury vapor at 1 bar) to a temperature of  $30,000^\circ$ ; (2) that this distribution is maintained even when the walls are negatively charged and hence are constantly removing the faster electrons; (3) that the number of collisions with

atoms and electrons is far too small to maintain this distribution, the mean free path being of the order of the tube diameter; (4) that mobility experiments indicate that the electrons suffer at least ten changes of momentum between consecutive collisions with atoms. A possible explanation of these results will be presented and discussed in Part IV below.

## II. ELECTRONS ACCELERATED FROM A HOT CATHODE

These Maxwellian distributions occur not only in ordinary low pressure arcs but are produced in gaseous discharges under many different conditions. We will now consider some experiments which have been made with spherical bulbs or cylindrical vessels containing a hot tungsten cathode and a disk-shaped anode. With gases at low pressures, currents of the order of ten milli-amperes and anode potentials of 50 to 250 volts, the space potential in the strongly ionized gas is nearly uniform and is somewhat above that of the anode. The cathode is surrounded by a positive ion sheath in which there is a sharp potential drop so that the electrons from the cathode are accelerated within a distance of a fraction of a millimeter, to a velocity exceeding that which corresponds to the potential difference between the anode and cathode.

Recently a very large number of experiments have been made by S. P. Sweetser, C. G. Found and H. A. Jones to investigate the production of these high speed electrons. A brief report of this work was made at the April meeting of the Physical Society<sup>6</sup> in Washington.

In one set of experiments (Exp. 548) a straight tungsten filament 1.1 cm long and 0.18 mm in diameter was mounted within about 2 cm of the center of a spherical bulb of 12 cm diameter. A disk-shaped collector 1.1 cm in diameter, backed by mica and movable in the direction of its axis, was mounted so that the axis passed through and was perpendicular to the filament at its center. The lead to the disk was insulated so that the collector could receive electrons only on the surface facing the filament. An anode was also placed in the bulb to one side of the line connecting the other electrodes.

By lighting the filament so that it emitted 5 milli-amperes and applying -50 volts to the cathode with respect to the anode (assumed to be at zero volts) the mercury vapor became strongly ionized and its potential was nearly uniform and equal to that of the anode. The electrons emitted by the filament acquired their full velocity within a few tenths mm and were therefore projected outwards in directions normal to the filament, thus forming a disk shaped "beam" of electrons. Those electrons

<sup>6</sup> Langmuir, Abstract in Physical Review 25, 891 (1925).

which reach the collector with a large part of the momentum which they acquired in passing through the positive ion sheath, we shall call *primary electrons*. The primary electrons in this beam which were intercepted by the collector were moving perpendicularly to its surface. To prevent these electrons from reaching the collector it was necessary to apply a potential lower than that of the cathode.

Thus, as the collector passed through the potential of the cathode, the current-voltage curve of the collector showed a sudden change in current which was a measure of the number of primary electrons which reached the collector without collisions. This discontinuity was very sharp when the cathode emission was only 5 m-amp. taking place within a range of only about 2 volts, which was not greater than would be expected because of such effects as the initial velocities of the emitted electrons and the voltage drop along the filament. Thus no appreciable number of electrons were present in the gas with velocities higher than those of the primaries.

*Scattering of primary electrons.* When the electron emission was raised to 10 m-amp. however, there were found to be unmistakable indications of the presence of electrons having velocities higher than the original primaries. Fig. 1 shows some typical data taken with 10 m-amp., with a cathode potential of  $-50$  volts, and a distance of 3 cm between filament and collector. The mercury vapor pressure was only 0.23 bar corresponding to saturated vapor at  $0^{\circ}\text{C}$ . The curve marked  $I_b$  gives the collector current in micro-amperes as a function of the collector potential. The curves  $0.1 I_b$  and  $0.01 I_b$  represent the same data on a scale 10 and 100 times smaller so as to bring the upper portions of the curve within the plot.

It is seen that at collector potentials below  $-60$  only positive ions are collected. The currents vary with the potential because of an "edge correction" which causes<sup>7</sup> the area of the positive ion sheath to increase as the sheath thickness increases. The dotted line  $A$  shows how this current would vary at higher potentials if no electrons were collected. At potentials above  $-59$  volts, at point  $M$ , electrons begin to be collected, showing the presence of appreciable numbers of electrons having energies of from 52 to 59 volts although the energy of the primaries was only 50 volts.

From the data of Fig. 1 we see that with the collector at  $-40$  at point  $N$  practically all the primaries have been collected. With a cathode current of only 5 m-amp. on the other hand, the primaries were all collected with voltages of about  $-47$ . This shows that the effect of raising the primary current from 5 to 10 m-amp. was to scatter the primary electrons,

<sup>7</sup> See loc. cit.<sup>2</sup>, p. 540.

causing not only an increase in the velocities of some of the primaries but a decrease in the velocity of others. The average energy of all the primaries was slightly lowered to about 47 volts. The total number of primary electrons collected was twice as great with 10 as with 5 m-amp. cathode current, so that the effective free path of the injected electrons remained

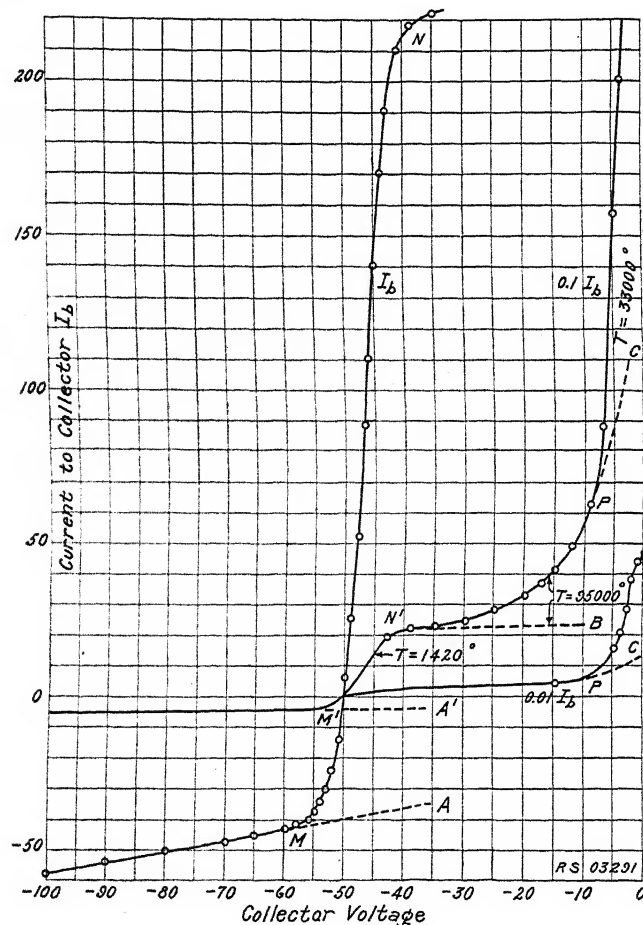


Fig. 1. Electron scattering in mercury vapor at 0.23 bar ( $0^\circ\text{C}$ ) with 10 m-amp. primary current and the cathode at  $-50$  volts.

the same, if by free path we mean the distance that the electrons travel before losing the greater part of their momentum in their original direction.

By subtracting from the observed currents (Fig. 1) the positive ion currents corresponding to the dotted line  $A$  we obtain the total electron current  $\Delta I_b$  to the collector. In Fig. 2 the logarithms of these currents in

micro-amperes have been plotted against the collector voltage. In this way the data for from  $-55$  to  $0$  volts are brought within a single convenient curve. The rise  $MN$  which occurs between  $-55$  and  $-40$  volts corresponds to the primary electrons. If these all had the original energy of  $50$  volts the rise should occur as a vertical line at an abscissa of  $-50$  volts. The inclination of the line from the vertical thus measures the amount of electron scattering.

The line  $N'B$  in Fig. 1, corresponding to the horizontal dotted line  $NB$  in Fig. 2, gives the current as it would be if no other electrons than the primaries were collected. The differences between the observed currents  $N'P$  and those of line  $N'B$  (Fig. 1) thus correspond to a new group of electrons which probably result from collisions of the primary electrons with gas molecules. We shall call these *secondary electrons*. This group includes primaries which have lost most of their energy and also electrons which are ejected from gas molecules by these collisions.

The distribution of velocities among the secondary electrons is found by taking the differences between the observed currents and the current corresponding to  $N'B$  (Fig. 1), and by plotting the logarithms of these differences as indicated by the points along the line  $D$  (Fig. 2). Within the range from  $-30$  to  $-12$  volts the points lie on a straight line. This proves that the velocity distribution follows Maxwell's law. From the slope the temperature of this secondary electron group is found to be  $95,000^\circ$ . By extrapolation to higher voltages along the straight line  $D$ , the currents corresponding to the secondary electrons are calculated as indicated by the dotted line  $PC$ . Thus the line  $NPC$  is the curve of the secondary electrons.

The difference between the observed currents  $PR$  and the secondary currents  $PC$  (Fig. 1) gives another group of electrons which we will see have a Maxwellian velocity distribution and are in fact the same as the free electrons found in the positive column of the low voltage discharge. We shall call these the *ultimate electrons*. If the currents due to these are small compared to the current flowing to the anode the logarithms of the currents may be plotted and the slope of the resulting straight line taken to measure their temperature. But, it often happens that the concentration of the ultimate electrons is so high that the current taken by the collector becomes comparable with that flowing to the anode. The collector may, in fact, rob the anode of nearly all its current and thus raise the space potential along with the collector potential. In these cases, as mathematical analysis shows, we should plot the logarithm of the ratio of the electron current to the collector, to the current to the anode. The slope of this line as indicated by line  $E$  measures



the temperature of the ultimate electrons. In view of the logarithmic scale of Fig. 2 it will be seen that the number of ultimate electrons greatly exceeds that of the primary or secondary electrons. The relative numbers of electrons in the various groups is seen more clearly in Fig. 1 because there the currents themselves are plotted as ordinates. The dotted lines  $N'B$  and  $PC$  on Fig. 1 are drawn to correspond to those in Fig. 2.

† In other experiments disk-shaped collectors were mounted close to the primary electron beam but in a plane perpendicular to the axis of the cathode so as to be parallel to the direction of the electron beam. The current to such a collector gives no indication whatever of the prim-

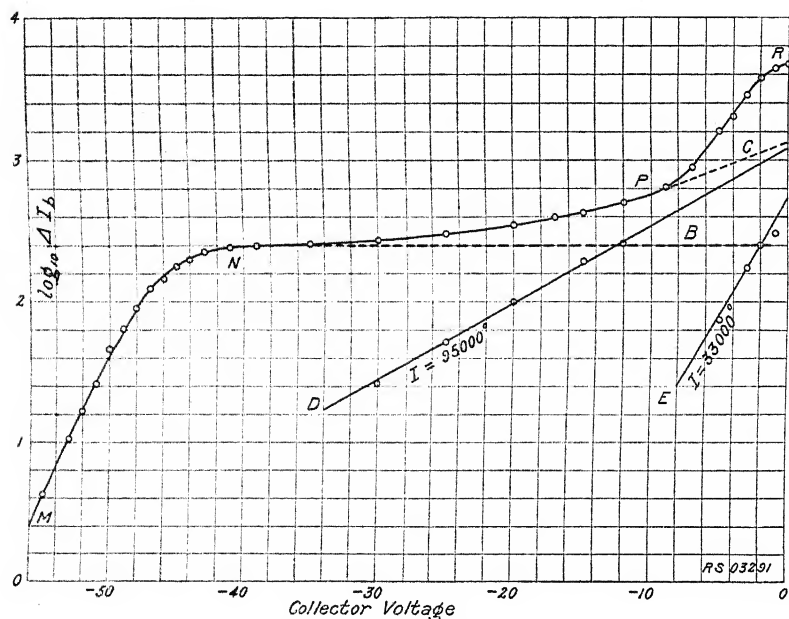


Fig. 2. Semi-logarithmic plot of the electron currents from the data of Fig. 1.

ary electrons corresponding to the rise  $MN$ , but the groups of secondary and ultimate electrons corresponding to the rises between  $NP$  and  $PR$  are exactly the same as those shown in Fig. 2 for a collector mounted perpendicular to the beam. Such experiments justify our separation of the electrons into groups of primaries and secondaries and establish the fact that the primaries move mainly in one direction while the secondaries and ultimate electrons move equally in all directions.

In our present discussion our interest centers on the *distribution of the velocities of the primary electrons* after they have passed through the ionized gas. The portions of the curves  $MN$  in Figs. 1 and 2 should give



us this distribution. In order to analyze such curves mathematically the hypothesis was made that the scattering of the primaries takes place in such a way that the resultant velocity distribution can be analyzed into a uniform translational velocity and a superposed Maxwellian distribution corresponding to a temperature  $T$ —this distribution being analogous to that of the molecules of a gas which is moving with uniform velocity.

We can now calculate what fraction of the electrons in such a beam can move against a given retarding field like that in the sheath of a negatively charged plane collector. Assuming that the velocities due to temperature motion are small compared to those of translation it can be shown that the current  $I$  of electrons which reaches a collector is given by

$$I = \frac{1}{2} I_0 (1 + \operatorname{erf} \beta) \quad (6)$$

where  $\operatorname{erf}$  denotes the error function

$$\operatorname{erf} x = \frac{2}{\sqrt{\pi}} \int_0^x e^{-x^2} dx. \quad (7)$$

$I_0$  is the current when all the primary electrons are collected and  $\beta$  is defined by the equation

$$\beta = (\sqrt{-V} - \sqrt{V_1}) / \sqrt{V_T}. \quad (8)$$

Here  $V$  is the potential of the collector with respect to the ionized gas (or anode),  $V_1$  is the potential corresponding to the translational velocity of the primary electrons and  $V_T$  is the potential corresponding to the energy  $kT$ ,  $k$  being the Boltzmann constant. If  $V_T$  is expressed in volts

$$V_T = T/11600. \quad (9)$$

When the collector potential is not too far from that of the cathode the value of  $\beta$  from Eq. (8) may be expanded giving

$$\beta = \text{const} + V/(2\sqrt{V_1 V_T}). \quad (10)$$

Thus  $\beta$  is a linear function of the collector potential and from Eqs. (6) and (10) we then see that  $\operatorname{erf}^{-1}[(2I - I_0)/I_0]$  is a linear function of  $V$  having a slope equal to  $1/(2\sqrt{V_1 V_T})$ . If this function of  $I$  is plotted against  $V$  and a straight line is obtained it proves the existence of the kind of velocity distribution we have assumed, and enables us to determine the temperature corresponding to the random part of the motion. These operations may be more conveniently carried out by using probability paper in which the vertical lines are uniformly spaced and the horizontal

lines, which are denoted by various values of a parameter  $a$ , are spaced according to the relation

$$y = \operatorname{erf}^{-1}(2a - 1)$$

*Temperature of primary electrons.* In Fig. 3 the primary electron currents corresponding to the data of Figs. 1 and 2 are plotted on probability paper. The abscissas are the collector voltages while the ordinates are  $\Delta I_b/I_0$  where  $I_0$  has been taken as 257 micro-amperes in accordance with the data of Fig. 1. It is seen that the observed points lie very close

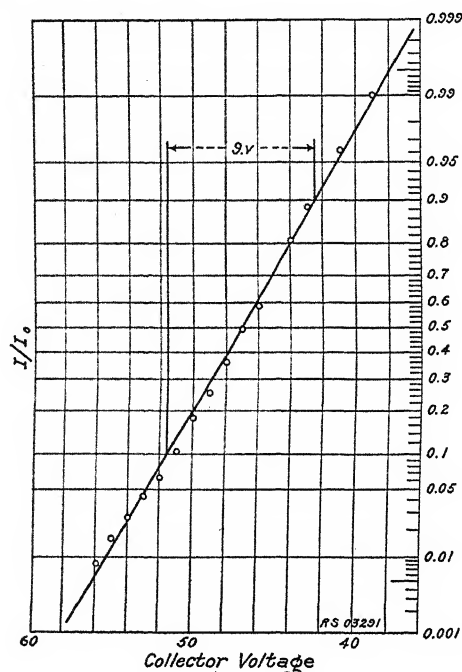


Fig. 3. Probability plot of the primary electron current from data of Fig. 1.

to a straight line. The difference in voltage corresponding to the 2 points  $I/I_0 = 0.1$  and  $0.9$  is  $9.0$  volts. The increment of  $\operatorname{erf}^{-1}(2a - 1)$  corresponding to these values is  $1.812$ . Thus by (10)

$$dV/d\beta = 9/1.812 = 2\sqrt{V_1 V_T}.$$

Since the energy of the primary electrons in the beam corresponds to  $50$  volts we place  $V_1 = 50$  and thus find  $V_T = 0.122$  volts or by (9)  $T = 1420^\circ$ . The voltage on the probability plot (Fig. 3) which corresponds to the midpoint (i.e. where  $I/I_0 = 0.5$ ) measures the average translational velocity of the electron beam. Thus from Fig. 3 the forward velocity of the

beam corresponds to 47.2 volts although the original velocity of the primary electrons corresponded to 50 volts. The mechanism producing the scattering therefore does not act uniformly in all directions but produces the greatest changes in momentum in a direction opposite to that of the original beam.

The data from large numbers of experiments, of which the data of Fig. 3 are typical, confirm the correctness of the hypothesis that the primary electrons have random Maxwellian velocities superposed upon the translational velocity. The degree of scattering in this case is very small as the voltage corresponding to the random velocities is only 0.122 while the voltage of the translational velocity is 47.

*Variation with current density.* To illustrate the effects produced by modification in the experimental conditions we may consider another typical run made with the same apparatus. The pressure of the mercury vapor was 1.6 bars corresponding to saturated vapor at 20°C. The electron emission from the cathode was 30 m-amp. The cathode was at a potential of -50 volts with respect to the anode, and the distance from the collector to the cathode was 3 cm as in the run illustrated in Figs. 1 to 3. The data were plotted and analyzed as before. Appreciable electron currents were observed with collector potentials as low as -90 volts showing that some electrons (about 3 micro-amperes) having energies as high as 90 volts had been produced from the original beam of 50 volt electrons. The secondary electrons gave a straight semi-logarithmic plot corresponding to  $T=95,000^\circ$  which is the same temperature as found from the data of Fig. 1. The temperature of the group of ultimate electrons was  $15,600^\circ$ . The plot of the primary electron current to the collector, on probability paper, gave 17 consecutive points in the voltage range from -90 to -10 volts which came very close to a straight line (maximum departure 3 volts) whose slope corresponded to  $T=56,000^\circ$ . The mid-point of this line was at -36 volts so that the beam had been retarded by an amount corresponding to 14 volts.

The very much higher temperature of the primary electrons in this experiment as compared to the previously described run is due mainly to the higher primary current density, but is partly due to the higher pressure of mercury vapor.

Fig. 4 illustrates the current-voltage curves of the collector for potentials below that of the cathode with a series of different primary current densities. The figures written near the curves are the electron emissions from the cathode in milli-amperes. Three different cathode potentials were used, -35, -50 and -70 volts. The actual experimental points

are indicated in only one curve, which being typical, illustrates the accuracy with which the observations fit the curves.

The moderately sloping parts of the curves, which are continued as dotted lines to the right, give the positive ion currents. The departures from these lines measure, as before, the primary electron currents. It will be noted that with 5 m-amp. the electrons begin to be collected only when the collector comes within 1 or 2 volts of the cathode potential, showing that there are very few electrons having higher velocities than those of the original primaries. As the current density is increased to

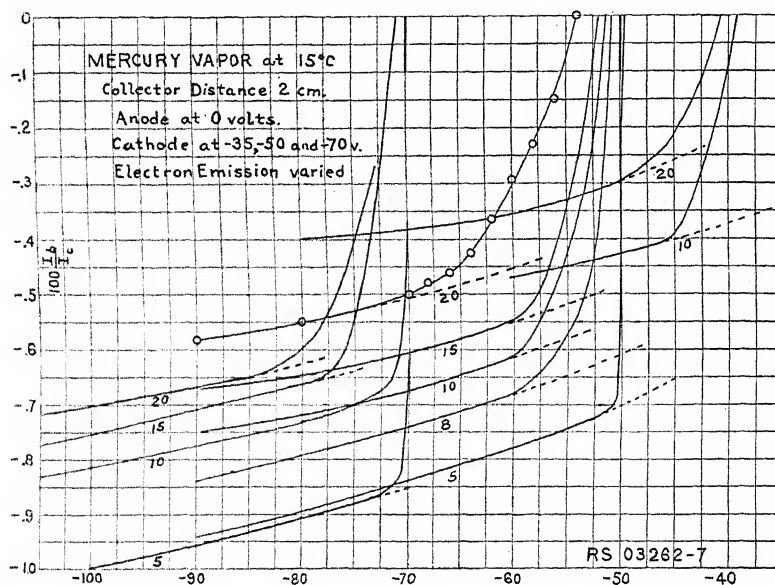


Fig. 4. The effects of cathode voltage and current density on the scattering of electrons. The ordinates give the ratio  $I_b/I_c$  where  $I_b$  is the negative current received by the collector and  $I_c$  is the electron emission from the cathode. The figures marking the curves are the values of  $I_c$  in milliamperes.

10 or 20 m-amp. however, electrons begin to be collected at potentials of 10 or even 20 volts below that of the cathode. The effect seems to be somewhat more marked at 35 and at 50 volts than at 70 volts.

In a series of later experiments the primary electron temperatures were determined for each of a series of primary current densities corresponding to electron emissions ranging from 3 to 30 m-amp. The mercury vapor pressure was 0.23 bars ( $0^\circ\text{C}$ ), the collector distance 3 cm, and the cathode potential  $-50$  volts. The primary electron temperature was found, within the experimental error, to be proportional to the  $2.2 \pm 0.2$  power of the current.

*Variation with the distance of the collector.* Experiments in which different distances between the cathode and the collector were used have shown that the primary electron temperatures increase roughly in proportion to the distance traversed by the electrons. Further experiments on this effect are in progress.

*Variation with cathode voltage.* In a series of experiments with mercury vapor at 0.23 bar (0°C) with a collector distance of 3 cm and a current of 10 m-amp. the primary electron temperatures varied with the voltage as follows:

voltage:	-80	-70	-50	-40	-35
$T$ :	800°	900°	1300°	1700°	2200°

With 20 m-amp. current, the other conditions being the same, the temperatures were

at -80 volts	at -50 volts
2050°	4750°

The greatest scattering of the electrons thus occurs at the lowest voltages, but, in general it is difficult and unsatisfactory to work with voltages below 50 volts because the effects of the scattering then tend to be masked by the secondary and ultimate electrons. As the voltage difference between cathode and anode decreases not only does the velocity of the primary electrons decrease but the character of the excitation of the ionized gas may change. For example, with higher voltage, atoms may be excited to higher energy levels. These experiments do not enable us to determine which of these factors is responsible for the change in the amount of scattering.

TABLE I

*Effect of mercury vapor pressure on electron scattering.*

Primary current (m-amp.)	Mercury Temp.	Mercury Pressure (bars)	Electron temperature	Retardation (volts)	$\frac{\Delta E_i}{\Delta E_r}$
10	0°	0.23	1360°	3.1	17.6
	20	1.6	870	2.3	20.4
	30	3.7	240	1.8	58.
	40	8.0	140	1.4	77.
20	0	0.23	5500	5.0	7.0
	5	0.37	7100	4.5	4.9
	10	0.61	9800	4.8	3.8
	15	1.0	5900	3.5	4.6
	20	1.6	4000	3.2	6.2
	35	5.5	750	1.8	18.5

*Variation with mercury vapor pressure.* Table I shows the way that the electron scattering varied with the vapor pressure of mercury. The cathode was at -50 volts and the collector distance was 3 cm. The last

column gives the retardation of the beam or the decrease in the translational energy of the beam as determined from the voltage of the mid-point of the straight line on the probability plot.

*Experiments with crossed beams.* The fact that the electron scattering is negligible at low current density and increases rapidly at higher currents suggests that it is caused by the action of radiation or by excited atoms or ions. To gain more information as to the effect of ionization and excitation of the gas a spherical bulb (12 cm in diameter) was provided with two straight cathode filaments, *A* and *B*, each 1.1 cm long, mounted in the same plane at right angles to each other. Facing these cathodes at distances of 4 cm there were disk-shaped collectors (*A'* and *B'*) of 1.1 cm diameter, the axes of these disks being in the same plane as the two cathodes.

By lighting only one cathode, *A*, a single disk-shaped beam of primary electrons (about 1 cm thick) was produced. The two collectors *A'* and *B'* being about the same distance from the center of the bulb, received the same number of secondary and ultimate electrons, but since *B'* was outside of the beam (and its surface was parallel to the direction of the beam) only the collector *A'* received primary electrons.

When both cathodes were lighted the volt-ampere characteristics of the two collectors gave the amount of scattering of each of the two perpendicular electron beams, and thus made it possible to determine the influence of one electron beam on the other.

It was found that the temperature and the number of both the *secondary* and the *ultimate* electrons were always very nearly the same for both collectors whether or not the collector was in the beam of primaries. The temperatures of both these groups were independent of the currents from the cathodes. The number of electrons in each of the 2 groups was a function of the sum of the currents emitted by the two cathodes and was in fact approximately proportional to this sum. Thus it was immaterial whether one cathode emitted 20 m-amp. while the other emitted none, or each of the cathodes emitted 10 m-amp.

The behavior of the primary electrons was entirely different. The total number of primaries that could be received by each of the two collectors was of course proportional to the electron emission of the opposing cathode. If the scattering of the primary electrons were due to the free electrons, or ions, or to the kind of excited atoms and radiation that is produced by the secondary and the ultimate electrons, we should expect that the temperatures of the primary electrons should be determined by the temperatures and the concentrations of these two groups of electrons.



Thus the temperatures of the primaries should also be a function of the sum of the emissions from the two cathodes.

The experiments showed, however, that the primary electron temperature depended mainly on the emission of electrons from the cathode which opposed the collector and was usually only slightly influenced by the emission from the other cathode.

For example, in some runs with mercury vapor at 0.75 bar ( $12^{\circ}\text{C}$ ) with both cathodes at  $-80$  volts, cathode *A* was heated to such a temperature that it emitted 5 m-amp. while *B* was adjusted to emit 20 m-amp. The temperature of the primaries reaching *A'* was  $800^{\circ}$  while those reaching *B'* had a temperature  $5200^{\circ}$ . When cathodes *A* and *B* were at the same temperature and each emitted 20 m-amp., the temperatures of the electrons received by each collector was still about  $5000^{\circ}$ . By then turning off the heating current to one of the cathodes, say *A*, so that its emission fell to zero, the temperature of the electrons received by the collector *B'* facing the other filament was practically unchanged notwithstanding the fact that the concentration of the secondary and ultimate electrons and of the positive ions throughout the whole space in the bulb, fell to about half value.

With mercury vapor pressures corresponding to  $20^{\circ}$  and especially to  $30^{\circ}\text{C}$  one beam of primary electrons seemed to be able to cause a distinct increase in the temperature of the other beam (which it intersected for about  $1/4$  of its length). For example, at  $30^{\circ}$  and with both cathodes at  $-80$  volts but only one cathode lighted so as to emit 20 m-amp., the electron temperature observed at the opposing collector was  $700^{\circ}$ . By allowing the other cathode also to emit 20 m-amp. both beams of primaries gave a temperature of  $2500^{\circ}$  thus showing a marked increase in temperature caused by the other beam. However, if one cathode was heated to emit 40 m-amp. while the other was cold the temperature of the beam was  $20,000^{\circ}$  or 8 times as high as when each cathode emitted 20 m-amp., although the concentrations of the secondary, and ultimate electrons was the same in the two cases. Evidently with mercury at  $30^{\circ}$  the exponent of the power of the current with which the electron temperature increases is higher than it is with vapor from mercury at  $0^{\circ}\text{C}$ .

From these results we may draw the definite conclusion that the main cause of scattering of 80 volt electrons, especially at low pressures of mercury vapor, is not the ionization, excitation or radiation produced by, or characteristic of the secondary or the ultimate electrons, but the scattering must be due to a more direct effect of the primary electrons and one which is confined to the region actually traversed by these primary electrons. This indicates that the scattering cannot be due to



electrons or ions per se. It leaves open, however, the question as to whether radiation or excited atoms may be the cause. Thus 80 volt primary electrons are capable of exciting mercury atoms to energy levels far above those obtainable from the secondary or the ultimate electrons, and radiations of correspondingly high frequency are similarly produced. Excitation and radiation of this kind might well be confined to the region traversed by the primaries and might thus explain the results of the experiments. The distinct but slight effect of one beam of electrons on the other would then be due to the action taking place within the region (about 25 percent of the total path) where the two beams intersect. Experiments are now in progress to study parallel beams and beams with intersect over nearly their whole lengths in order to clear up this question.\*

In some other experiments an arc of 0.2 to 0.5 ampere was passed through mercury vapor in a 12 cm bulb from an external mercury cathode while the distribution of the velocities of 50 volt primary electrons from a hot cathode in the bulb was studied. It was found that the ionization due to the arc did not increase the primary electron temperatures.

### III. MECHANISM OF ELECTRON SCATTERING

Before taking up this general problem, let us enquire whether the scattering of the electron beam can be due to encounters with other electrons. Since the electrons in the beam start out from the cathode with the same velocity, they have no velocity with respect to one another and therefore cannot deliver energy to one another by collision. Space charge due to the electrons in the beam is neutralized by positive ions, but even if it were not, the electric field due to space charge could produce only transverse scattering and would not change the longitudinal velocities of the electrons.

*Scattering by clouds of stationary electrons.* If the scattering is to be produced by electrons, it must be due to the electrons in the ionized gas and these as we have seen have velocities much lower than those of the primaries. Let us therefore consider the scattering of a beam of electrons when it enters a cloud of stationary electrons. If we assume that the collisions follow the laws of elastic spheres we find that an electron which

\* *Note added Sept. 2, 1925.* In some recent experiments two straight tungsten filaments 1 cm long were mounted parallel to one another at a distance of about 1 mm, so that two electron beams could be obtained that were practically coincident. In this case the primary electron temperature depended only on the *sum* of the electron emissions from the two cathodes, showing that the scattering did not occur within the cathode sheath but resulted from some effect taking place throughout the space traversed by the primary electrons.

has made one collision with a stationary electron has on the average lost one half its momentum in the forward direction and has given half its energy to the other electron. Thus, if we have a beam of electrons which are moving with a homogeneous velocity corresponding to a voltage  $V_0$  and we let this beam encounter a cloud of stationary electrons so that each electron in the beam makes one collision with an electron, we find that the translational velocity of the beam is reduced to a value corresponding to  $\frac{1}{4}V_0$ . An observer, moving along with this retarded beam, will see that the electrons in the beam are now moving in random directions with velocities corresponding to the energy  $\frac{1}{4}V_0$ . The effect of a single collision for each electron thus causes a decrease in the longitudinal energy of the beam of  $\Delta E_l$  and an increase in the *random* energy  $\Delta E_r$  given by

$$-\Delta E_l = \frac{3}{4}V_0e \quad (11)$$

$$\Delta E_r = \frac{1}{4}V_0e \quad (12)$$

the ratio being

$$-\Delta E_l/\Delta E_r = 3 \quad (13)$$

The electrons in the retarded beam cannot, however, in this case get a Maxwellian velocity distribution. There is no mechanism by which an electron can acquire velocities exceeding those in the original beam. If the number of electrons in the cloud is so small that the average decrease in the longitudinal energy is say 5 percent (about the average observed in our experiments) then 93.3 percent of the electrons have made no collisions at all and must retain all their original translational energy while 6.7 percent have lost 3/4 of their original energy. This would give a velocity distribution having no resemblance to a Maxwellian distribution. Thus we must conclude that the observed scattering cannot be due to the direct action of electrons upon those in the beam.

*Scattering by clouds of entities of very small mass.* If the particles in the cloud have masses  $m_p$  negligibly small in comparison to those of electrons, these difficulties disappear. In this case the fractional decrease in the translational velocity  $v_l$  of an electron in the beam is<sup>8</sup>

$$-\frac{\Delta v_l}{v_0} = \frac{4}{3} \frac{m_p}{m} n \quad (14)$$

where  $n$  is the number of collisions, and  $v_0$  is the original velocity of the electrons in the beam. The decrease in longitudinal energy is thus

$$-\Delta E_l = \frac{4}{3} m_p v_0^2 n = \frac{8}{3} (m_p/m) n V_0 e. \quad (15)$$

<sup>8</sup> See Eq. (789) in Jeans' *Dynamical Theory of Gases*, 2nd Edition, p. 282. Cambridge, 1916.

A particle of velocity  $v_p$  colliding with an electron in the beam delivers its whole momentum  $m_p v_p$  to the electron and the energy  $E$  thus acquired by the electron is

$$E = (m_p/m) E_p \quad (16)$$

where  $E_p$  is the kinetic energy of the particle. Since the energy of the particles which *strike* the electron is  $2kT_p$  we have for the average random energy after  $n$  collisions

$$\Delta E_r = 2nkT_p (m_p/m). \quad (17)$$

This average energy corresponds to  $\frac{3}{2}kT$  so that the temperature of the primary electrons after  $n$  collisions is

$$T = \frac{4}{3} n T_p (m_p/m). \quad (18)$$

By comparing Eqs. (15) and (17) we find for the ratio of the decrease in longitudinal energy to the increase in random energy

$$\frac{-\Delta E_l}{\Delta E_r} = \frac{4}{3} \frac{V_0 e}{k T_p}. \quad (19)$$

For convenience we may express  $T_p$  in terms of the equivalent voltage  $V_p$  defined by

$$V_p e = k T_p \quad (20)$$

so that (19) becomes

$$\frac{-\Delta E_l}{\Delta E_r} = \frac{4}{3} \frac{V_0}{V_p} \quad (21)$$

*Scattering by quanta.* The momentum of a quantum of energy  $h\nu$  is  $h\nu/c$ . If this quantum acts on an electron it may deliver to the electron any momentum between 0 and  $2h\nu/c$  according to the direction taken by the scattered quantum. If the quanta are scattered with equal probability in all directions, as if by elastic spheres, the average momentum transferred may be taken to be  $h\nu/c$ . The average energy delivered to the electron by  $n$  collisions is

$$E_r = \frac{2}{3} n (h\nu)^2 / mc^2. \quad (22)$$

Thus after  $n$  collisions with quanta the electron temperature is

$$T = (4/9) n (h\nu)^2 / k mc^2. \quad (23)$$

We may conveniently express the energy of the quanta  $h\nu$  in terms of the equivalent voltage  $V_q$  according to the relation

$$h\nu = V_q e. \quad (24)$$

Introducing the numerical values of  $k$ ,  $m$ ,  $c$  and  $e$  and expressing  $V_q$  in volts, Eq. (23) thus reduces to

$$T = 0.0102nV_q^2. \quad (25)$$

Thus, for example, with quanta of a frequency corresponding to 50 volts, the temperature of the electrons increases by  $25^\circ$  for each collision with quanta.

The fractional decrease in drift velocity of the electrons after  $n$  collisions with quanta is

$$-\Delta v_{L1}/v_0 = 4n\hbar\nu/3mc^2 = 2.62 \times 10^{-6}nV_q \quad (26)$$

and the decrease in longitudinal energy is thus

$$-\Delta E_L = 4v_0^2n\hbar\nu/3c^2 = \frac{4}{3}(v_0/c)^2nV_qe. \quad (27)$$

Comparing this with (22) we find

$$-\Delta E_L/\Delta E_r = 4V_0/V_q. \quad (28)$$

*Relation between the retardation and the scattering.* Let us compare these calculated values of  $\Delta E_L/\Delta E_r$  with the results of the experiments. In the experiment for which data were given in Fig. 1 the retardation corresponded to 2.8 volts and the electron temperature, due to scattering, was  $1420^\circ$ . The average energy in random direction  $E_r$  corresponds to  $\frac{3}{2}kT$ , so to express  $E_r$  in volts we divide the temperature by  $2/3$  of 11600, or 7730. Thus we find  $-\Delta E_L/\Delta E_r = 15.3$ ; i.e., the loss of energy by retardation is 15.3 times as great as the thermal energy of the scattered electrons.

Comparing this result with Eq. (28), we find  $V_0/V_q = 3.8$ , and therefore  $V_q = 13$  volts since  $V_0 = 50$  volts. Thus, quanta of a frequency corresponding to 13 volts would produce the ratio of retardation to scattering which was found by the experiments.

Rather variable results are obtained from other experiments. For example, the last column of Table I gives values of  $-\Delta E_L/\Delta E_r$  ranging from 3.8 to 77, which would correspond to quanta having frequencies corresponding to voltages  $V_q$  from 53 down to 2.7. These values are all of reasonable order of magnitude, since radiation of such frequencies may well be present in gases excited by electrons of 50 volts energy.

If we assume that the scattering occurs according to the laws of the kinetic theory, by Eq. (21), the voltages corresponding to the energies of the particles will be  $1/3$  of those just found for  $V_q$ . These values also seem possible, although less probable, and we therefore cannot decide between the two theories from these data. Since, however, no entities

other than quanta are known having masses less than those of electrons, we will confine our attention at present to scattering by radiation.

*Magnitude of Compton effect.* According to the classical electromagnetic theory<sup>9</sup> the scattering coefficient of light by free electrons is

$$\alpha = 6\pi a^2 n_e \quad (29)$$

where  $\alpha$  is the fraction of energy scattered per unit length of path through a region occupied by  $n_e$  electrons per unit volume and  $a$  is the radius of the electron by Lorentz's theory ( $a = 1.88 \times 10^{-13}$  cm). Thus we find

$$\alpha = 6.7 \times 10^{-25} n_e \text{ per cm.} \quad (30)$$

According to the correspondence principle, we should expect approximately this amount of scattering even if the scattering takes place by quanta. For metallic aluminum  $n_e = 8 \times 10^{23}$  electrons per  $\text{cm}^3$ , so we obtain  $\alpha = 0.53$  per cm, which gives a scattering of the order of magnitude found for the Compton effect.<sup>10</sup> For a mercury arc  $n_e$  is of the order of  $10^{10}$  electrons per  $\text{cm}^3$ , so that  $\alpha$  should be about  $10^{-14}$ . This is in accord with the fact<sup>11</sup> that no Tyndall cone is observed when a strong beam of sunlight is focussed by a large lens into a nearly non-luminous 2-ampere arc in argon at a few millimeters pressure.

With a primary electron current of 10 m-amp. and 50 volts, the total energy escaping from the disk-shaped electron beam is about 0.02 watt per  $\text{cm}^2$ , or about  $5 \times 10^{15}$  quanta ( $V_q = 25$  volts) per  $\text{cm}^2$  per second. With a scattering coefficient of only  $10^{-14}$  there would be 50 quanta scattered per  $\text{cm}^3$  per second. To give the observed electron temperatures of  $1420^\circ$  each electron would have to make (according to Eq. 25) 230 collisions with quanta. Since there are  $6 \times 10^{16}$  electrons per second in the primary beam, the number of collisions per second would need to be  $1.5 \times 10^{19}$  or about  $3 \times 10^{17}$  per  $\text{cm}^3$  per second, instead of the 50 collisions calculated above.

Thus, the observed scattering is about  $10^{16}$  times greater than that to be expected from a normal Compton effect.

This difficulty seems to be very similar to that met with in connection with the theory of chemical reaction velocity<sup>12</sup> where it is found that a chemical molecule must become activated millions of times more frequently than it collides with other molecules. Yet the energy that it can

<sup>9</sup> Leigh Page, *Astrophysical Jour.* **52**, 67 (1920).

<sup>10</sup> Since the frequencies of x-rays are sufficient to remove most of the electrons in aluminium, we may consider the electrons as free electrons in regard to the scattering of this kind of radiation.

<sup>11</sup> According to rough experiments in this laboratory.

<sup>12</sup> Langmuir, *Jour. Amer. Chem. Soc.* **42**, 2190 (1920).

receive by radiation, according to the usual radiation laws, is millions of times too small to cause this activation.<sup>13</sup>

*Scattering by the joint action of radiation and excited atoms.* Because of the small magnitude of the Compton effect we must conclude that the scattering of electrons is not due to any direct interaction between them and radiation. It may well be, however, that the effect is due to an *interaction between radiation, excited atoms and electrons*.

Resonance radiation is enormously strongly scattered by excited atoms, practically all the radiation coming within a distance of about one-half wave-length from an excited atom being scattered, whereas the radiation scattered by an electron is only 6 times that falling on an area equal to the cross-section of the electron. For radiation corresponding to 25 volts the wave-length is 490A. The radiation scattered by an excited atom of a 25 volt energy level is thus about  $10^{14}$  times greater than that scattered by an electron. This is about the order of magnitude of the ratio ( $10^{16}$ ) of the observed scattering to that calculated for a normal Compton effect. If resonance radiation is trapped within the region traversed by the primary electrons, the ratio  $10^{16}$  would be reduced, so that it might well be brought down to the value  $10^{14}$  corresponding to the radiation scattered by excited atoms.

When a quantum of resonance radiation is scattered by an atom or excited atom the direction of the quantum is changed and the difference of momentum is available to deliver an impulse to some particle. Although we would expect in general that the momentum would be delivered to the atom or excited atom, it may well be that if an electron is close enough, the momentum may be delivered to the electron. In some such way as this we may suppose that the electrons can receive momenta whose magnitude is in accord with Compton's theory, although the probability that an electron may receive this momentum is  $10^{14}$  times greater than according to the normal Compton effect.

Consider the excitation of a mercury atom by a quantum of resonance radiation ( $\lambda 2537$ ). The difference in the angular momentum of the atom before and after excitation must be a multiple of  $h/2\pi$ . Before the encounter, the two-body system, consisting of atom and quantum, will also contain an angular momentum equal to the product of the momentum  $h\nu/c$  of the quantum, by the distance between the center of the atom and the path of the quantum. This angular momentum in general will not be a multiple of  $h/2\pi$ . After the collision we have a one-body system having a fixed angular momentum. Thus, it would seem that a

<sup>13</sup> See also a recent paper by R. C. Tolman, Jour. Amer. Chem. Soc. **47**, 1524 (1925).

<sup>14</sup> Barkhausen and Kurz, Phys. Zeits. **21**, 1 (1920).



mercury atom can be excited by a quantum only if a third body is present which can take up the residual angular momentum. An electron within a distance comparable to a wave-length may serve as such a third body and may thus increase the ease with which excited atoms are formed. Perhaps without such third bodies, resonance radiation cannot even be scattered, although it is not necessary to draw this conclusion, since scattering involves a two-body problem both before and after the scattering. Experiments to determine whether the scattering coefficient of resonance radiation is dependent on the presence of free electrons are in progress by Mr. Whitten in this laboratory. An attempt will also be made to determine whether low velocity electrons in mercury vapor or sodium vapor are scattered when resonance radiation is allowed to act on the vapor.

The loss of energy by retardation of a beam of primary electrons is always much greater than the energy that appears as thermal energy of the scattered electrons. A beam of primary electrons may thus deliver energy directly to the radiation, or to excited atoms, by the reverse of the process that causes scattering of the electrons. Thus the average frequency of the radiation in the primary beam probably increases as the current density of the beam is raised. This may be the reason that the primary electron temperature increases with the square or even with a higher power of the current density.

As an alternative hypothesis to account for the large amount of electron scattering, we may assume that the presence of an electron within a distance comparable to a wave-length from an excited atom, greatly increases the probability that the excited atom will emit a quantum of radiation. Thus, the average intensity of radiation near the electron would be much greater than that in the space as a whole and the magnitude of the Compton effect would thereby be increased. The momentum delivered to the electron in this case may, however, be very much greater than that due to a Compton effect. Of course, if an electron increases the probability of emission of radiation by an excited atom it must also increase the probability of the absorption of a quantum by an atom according to the reverse process. If scattering of resonance radiation is due to quantum jumps then, the scattering should be increased by the presence of electrons.

#### IV. EXPLANATION OF MAXWELLIAN DISTRIBUTION OF ULTIMATE ELECTRONS

We have seen that the primary electrons from a cathode at  $-50$  or  $-80$  volts are scattered mainly by some direct effect of the primary



electrons and not by the action of the ionization or excitation caused by the secondary or the ultimate electrons. In the positive column of an arc primary and secondary electrons are absent. It might seem, therefore, that the mechanism by which the electrons in an arc acquire their Maxwellian distribution must be different from that which causes the scattering of primary electrons. It seems more probable, however, that the mechanism is essentially similar, the difference being merely one of degree.

For example, in an arc in mercury vapor at 5 bars pressure the temperature of the ultimate electrons is about  $20,000^\circ$ , corresponding to an average energy ( $\frac{3}{2}kT$ ) of 2.6 volts. According to Eq. (25) the corresponding radiation ( $\lambda 4700$ ) would increase the temperature of electrons by only  $0.08^\circ$  for each quantum scattered, whereas 50 volt radiation which might exist in the primary beam could raise the temperature by  $25^\circ$  per collision.

In the case of the ultimate electrons in an arc it seems probable that there is a kind of thermal equilibrium between the electrons and the radiation and excited atoms. That is, the electrons lose as much energy to the radiation on the average, as they gain from it. Thus there is probably a definite relation between the temperature of the ultimate electrons and the frequency of the ultraviolet radiation or the average energy levels of the excited atoms.

The effective electron free-path determined from the mobility of electrons in an arc is not the average distance the electron moves before being acted on by a quantum, but is the distance it must move before losing most of its momentum in a given direction. By Eq. (26) we see that an electron will lose about half its forward momentum when it has made 190,000 collisions with quanta of a frequency corresponding to 2.6 volts. The experiments have given an effective free path of about 3 cm at one bar so the distance between successive interactions with quanta would average  $1.5 \times 10^{-5}$  cm.

It will be understood that the foregoing theoretical considerations are purely tentative. The fundamental cause of electron scattering can be established only after further experimental studies of the laws governing it.

## V. SCATTERED ELECTRONS IN HIGH VACUUM TUBES.

One of the most striking characteristics of electron scattering is the ability of some electrons to pass to an electrode which is more negatively charged than the cathode from which the electrons originate. A similar phenomenon is observed in vacuum tubes having apparently the highest

vacuum if the anode consists of one or more wires of small size at high positive potential while a surrounding cylindrical electrode is negatively charged with respect to the cathode. A current of electrons flows to this cylinder. This effect, discovered by Barkhausen and Kurz<sup>14</sup> was explained by them as being due to electrical oscillations of electrons in the evacuated space. These oscillations were actually detected by Barkhausen and Kurz. Gill and Morell<sup>15</sup> have outlined a theory which suggests a cause of the oscillations.

Experiments in this laboratory, however, have shown that although oscillations frequently exist in such a tube they do not seem to be the sole cause of the currents to the negative cylinder. For example, in some experiments the logarithm of the current to the cylinder varied linearly with voltage on the cylinder suggesting a Maxwellian distribution of the high speed electrons in the space. The temperature of these electrons was found to be proportional to the potential on the anode. With cylinder potentials close to those of the cathode electrical oscillations were observed, but when the cylinder was made more strongly negative the oscillations stopped abruptly and completely as far as could be determined, and simultaneously the current to the negative cylinder *increased* several fold.

Similar effects are observed in a magnetron having end plates charged negatively with respect to the cathode. A longitudinal magnetic field tends to prevent electrons from reaching the cylindrical anode and the negative potentials on the end plates tend to prevent their escaping at the ends of the cylinder. Under these conditions, small currents of electrons do flow to the cylinder in spite of the magnetic field and flow to the end plates even if these are 20 to 50 volts negative with respect to the cathode. Yet oscillations can very rarely be detected. These experiments have been repeated by Mr. C. G. Found with the very best vacuum conditions using an anode of deposited magnesium on the glass wall and immersing the whole apparatus in liquid air, but the currents to the negative electrodes were not decreased.

It will be noted that these effects might be explained if the trapped electrons in the Barkhausen-Kurz tube or in the magnetron were scattered so as to obtain a Maxwellian distribution. However, it is hard to see how this distribution can be brought about with so few excited atoms and so little radiation as must be present in these tubes.

<sup>15</sup> Gill and Morell, *Phil. Mag.* 44, 161 (1922).

VI. OSCILLATIONS AS A POSSIBLE CAUSE OF SCATTERING  
IN IONIZED GASES

Since oscillations occur so often in tubes of this character and have been suggested as a cause of the currents to negative electrodes, it has been felt throughout the experiments on the scattering of electrons in ionized gases, that it is important to determine whether oscillations are present. For this reason we have frequently used radio detectors capable of detecting oscillations of 0.5 meter wave-length and have introduced small capacities and inductances in various parts of the circuits to see if any of the currents to collectors could be modified in this way. In none of the experiments on electron scattering in low pressure gases using hot cathodes have oscillations been observed. In some experiments with mercury arcs oscillations occurred at first until high resistances or choke coils were used in the anode circuits. The effects produced by the oscillations were not at all like those characteristic of electron scattering.

RESEARCH LABORATORY,  
GENERAL ELECTRIC CO.,  
SCHENECTADY, NEW YORK,  
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RELATIVE PRODUCTION OF NEGATIVE AND POSITIVE IONS BY ELECTRON COLLISIONS<sup>1</sup>

BY F. L. MOHLER

## ABSTRACT

In the tube used, either positive or negative ions produced by an axial beam of electrons accelerated from a filament by a voltage  $V$ , were collected on a concentric cylindrical electrode  $D$  by maintaining it at a potential slightly lower or higher than that of the beam, the primary electrons being prevented from reaching  $D$  by means of a solenoidal magnetic field of 100 gauss parallel to the axis. While saturation was not always reached, the relative values of the positive and negative ion currents are significant. Contrary to the ordinary theory, the polar compounds *mercuric chloride* and *hydrogen chloride* gave results quite similar to those for the elements *mercury* and *iodine*. With electron currents of the order of  $10^{-6}$  amp. and pressures of about .001 mm, the negative ion current is in all cases small compared with the positive ion current above the ionization potential. With larger currents the negative current increases sharply at the ionization potential and the ratio to positive current is greater. For vapors other than mercury there are some negative ions produced at all voltages, the negative ion currents each having a maximum at zero and increasing again at certain critical potentials, the voltages being 4 for  $\text{HgCl}_2$ , 6.5 for  $\text{HCl}$  and 2.4, 4.6, 8.4 for  $\text{I}_2$ . As far as is known, these potentials are equal to *potentials of inelastic collision*. These experiments give no support to the theory that electron collisions dissociate polar molecules into positive and negative ions. In agreement with the results of the magnetic analysis of positive ions, they indicate that the primary effect of an electron impact is the production of a positive molecule ion. The negative ion curves obtained can be explained by the hypothesis that only slow moving electrons attach themselves to molecules to form ions, but the absence of low voltage negative ions in the case of  $\text{Hg}$  is not understood.

IT is generally assumed that negative ions are produced by electron collision in two different ways, by an electron attaching itself to a neutral molecule, and by an electron collision splitting the molecule into a positive and negative ion.

Measurements<sup>2</sup> of electron mobility indicate that some normal molecules readily form ions by attachment of electrons, notably chlorine and oxygen, while hydrogen, nitrogen and the rare gases show complete absence of negative ion formation. On the other hand electromagnetic resolution of the ions formed in an electric discharge shows the presence

<sup>1</sup> Published by permission of the Director of the Bureau of Standards of the U. S. Department of Commerce.

<sup>2</sup> Loeb, *Phil. Mag.* **43**, pp. 229-236 (1922).

of negative ions in other gases including those just excepted.<sup>3</sup> The experiments are not contradictory, however, for Franck and Grottrian<sup>4</sup> have pointed out that atoms or molecules in excited states will have properties entirely different from normal molecules and in some states may well have a strong electron affinity. Mobility measurements are made under conditions insuring almost complete absence of excited molecules while quite the contrary is true in the experiments involving electromagnetic analysis of the ions.

The assumption that electron collisions may dissociate molecules into positive and negative ions is based on the numerical agreement between the computed work required to so dissociate polar molecules and the observed ionization potentials. The hydrogen halides offer the only instance where the data compared are entirely satisfactory and the agreement in these instances is remarkably good. Table I gives some results. It has, however, been questioned whether these data give conclusive proof as to the nature of the ionization process.<sup>5</sup>

TABLE I  
*Ionization of hydrogen halides.<sup>6</sup>*

Halide	Work to separate ions	Observed ionization potentials		
		(Knipping)	(Mackay)	(Foote and Mohler)
HCl	13.7	13.7	13.8	14.0
HBr	13.1	13.3	13.2	
HI	12.7	12.7	12.8	

The methods of electromagnetic analysis have recently been applied to the low voltage thermionic discharge and important information is being obtained on the minimum potentials required to produce positive ions of known  $e/m$  ratio.<sup>7</sup> An inherent limitation of the method makes it difficult, however, to measure the formation of negative ions as a function of the voltage. In the method here described use is made of a magnetic field merely to separate the heavy ions from the electrons.

#### EXPERIMENTAL METHOD

Fig. 1 indicates diagrammatically the arrangement of electrodes in the electron tube used. The filament *A* and the diaphragms *B* produce a beam of electrons which passes along the axis of the cylindrical electrode *D* to the wire gauze electrode *C* and plate *C'*. A helix around the entire

<sup>3</sup> J. J. Thompson, "Rays of Positive Electricity" p. 70 et seq.; Smyth, Proc. Roy. Soc. 104A, 121 (1923).

<sup>4</sup> Franck and Grottrian, Zeits. f. Phys. 4, 89-90 (1921).

<sup>5</sup> Mackay, Phys. Rev. 24, 319 (1924).

<sup>6</sup> Compton and Mohler, "Critical Potentials and Their Interpretation," Bull. Nat. Res. Coun. No. 9, p 112 (1924).

<sup>7</sup> Smyth, J. Frank. Inst. 198, 795-811 (1924); Phys. Rev. 25, 452 (1925).

tube gives a magnetic field  $H$  of about 100 gauss parallel to the axis and to the electron beam. For ion measurements potentials are applied as indicated in the figure. The electron speed is determined by the variable potential difference  $V$  and  $V_2$  is a relatively small potential, usually  $\pm 1$  volt, which draws the ions to the receiving electrode. The electrons move in a nearly equipotential region and in the absence of a magnetic field any gas in the tube will tend to scatter them to the side electrode. The current from scattering was found to be large compared with the ion current, a result in accord with published data<sup>8</sup> on scattering and ionization. In argon at 25 volts the probability of scattering is 10 times that of ionization and at 17 volts about 100 times as great. The function of the magnetic field is to prevent this scattered current reaching the side electrode.

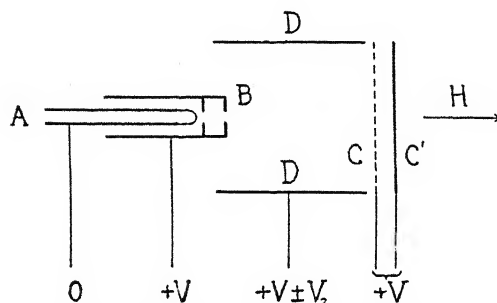


Fig. 1. Arrangement of electrodes and method of applying potentials for measuring either positive or negative ions. The arrow  $H$  indicates the direction of the magnetic field.

Electrons<sup>9</sup> having a velocity corresponding to a potential of  $V$  volts moving in an equipotential space at right angles to a magnetic field  $H$  will describe circles of radius

$$R = 3.4 \sqrt{V}/H.$$

In the form of tube here used an electron moving along the axis is unaffected by the magnetic field but if it is deflected by a single molecular collision through an angle  $\theta$  it will move in a helix of radius

$$R = (3.4 \sqrt{V}/H) \sin \theta.$$

This helix is tangent to the axis so that the electron departs from the axis a maximum distance  $2R$ . Electrons scattered at  $90^\circ$  reach a distance  $6.8\sqrt{V}/H$  from the axis. Ten-volt electrons in a field of 100 gauss will after a single scattering move on helices within .2 cm of the axis.

<sup>8</sup> A. L. Hughes, "Collisions between electrons and molecules," Washington Univ. Studies 11, 117-152 (1924).

<sup>9</sup> Hull, Phys. Rev. 18, 34 (1921), gives equations for the motion of electrons in superposed electric and magnetic fields for various electrode shapes. This paper and one by Richardson and Chaudhuri, Phil. Mag. 45, 337-52 (1923), include some experimental results on the effect of a trace of gas on the motions.



The radius of the cylinder  $D$  was about 1.5 cm. An ion of mass 35 relative to hydrogen and with a velocity corresponding to one volt will move on a path with a radius of curvature of about 9 cm. It follows that with the conditions here used the scattering of electrons to the side electrode can be prevented without seriously affecting the motion of the heavy ions.

The magnetic field introduces one complication. Without the field the diaphragms  $B$  limit the current to electrons which move along the axis. In the presence of the field electrons move on helices tangent to the axis so that electrons starting at angles of  $\theta$  between  $0^\circ$  and  $90^\circ$  may be able to pass through the diaphragms. An electron which starts at an angle  $\theta$  and velocity  $v$ , moves along the axis with a speed  $v \cos \theta$  and traverses a path of length  $1/\cos \theta$  in unit distance along the axis. The stopping potential at a surface normal to the axis will be  $V \cos^2 \theta$ . Curves of retarding potential between  $C$  and  $C'$  versus current reaching  $C'$  indicate that actually many electrons had large values of  $\theta$ . The form of the electrodes precludes detailed mathematical analysis but it seems probable that the average value of  $\theta$  and hence the average length of electron path will vary with the voltage so that quantitative conclusions concerning the production of ions at different voltages cannot be drawn.

To avoid multiple electron collisions and other complicating effects, these experiments were limited to low pressures (less than .01 mm) and small electron currents (between  $10^{-5}$  and  $10^{-6}$  ampere). The positive ion currents were of the order of one percent of the electron current. The construction of the electron tubes was modified in various details during the course of the work but with no important effects on the results.

The tubes showed the following characteristics. The curve of electron current to  $CC'$  versus  $V$  rose rapidly from near the origin in the first few volts and reached a nearly constant value above 6 or 8 volts. The curve of positive ion current to  $D$  as a function of  $V_2$  rose sharply from a point between  $+.55$  and zero volts and reached saturation at a negative potential of 2 volts or more. Only at the lowest pressures and currents did the ion current at  $V_2 = -1$  approximate the total production of ions. A 50 percent change of the magnetic field in either direction had little effect on the ion current.

Vapor pressures of iodine and mercury were controlled by the temperature of a side tube in which they were contained while the pressure of  $\text{HgCl}_2$  was determined by the temperature of the main tube.  $\text{HCl}$  was streamed through a fine capillary tube from a reservoir containing gas at pressures between 76 and 10 cm.



## EXPERIMENTAL RESULTS

Figs. 2 to 4 show currents to  $D$  as a function of the voltage  $V$  applied to the electron current, except that curves marked  $SP$  give electron currents reaching  $C'$  against a retarding potential between  $C$  and  $C'$ , the potential  $V$  being constant. Positive ion currents to  $D$  at  $V_2 = -1$  volt are indicated by  $P$ , negative ion currents with  $D$  at  $V_2 = +1$  volt, by  $N$ . The current per unit electron current would give a curve of different shape in the first few volts. Table II gives data on experimental conditions for these curves. Initial potential corrections were made on the basis of published measurements of ionization potentials. Table III lists the reference values as well as observed values of other potentials relative to these.

TABLE II

*Currents\* and pressures\* for curves of Figs. 2, 3 and 4.*

Vapor	Curve number	Pressure (mm)	Electron current ( $10^{-6}$ amp.)	Pos. ion current ( $10^{-8}$ amp.)	Neg. ion current ( $10^{-8}$ amp.)	Pot. $V$ for current meas.
Hg	PII, NII	.001	.95	2.3	.1	18 volts
	PI, NI	.002	.92	3.7	.6	18
HgCl <sub>2</sub>	PI, NI	<.003	2.0	3.7	.3	16
	NII	<.003	6.0	....	3.4	16
H Cl	PIV, NIV	.0005	3.2	1.1	.07	18
	PIII, NIII	.001	2.9	2.3	.34	18
	PII, NII, NI	.001	7.5	16	5.5	18
	NV	.002	4.3	(24)	7.7	18
I <sub>2</sub>	PIII, NIII	.002?	12.6	2.8	.38	15
	PI, NI	.01	6.9	22	9.5	15
	NII	.01	(3.5)	(120)	....	15

\* Values in parentheses are from data not plotted. Pressures are in general not accurate.

TABLE III

*Critical potentials for production of ions.*

Vapor	For positive ions	For negative ions
Hg	10.4*	10.4
HgCl <sub>2</sub>	12.1*	12.1
		4.
HCl	13.8*	13.8
		6.5
I <sub>2</sub>	10.0*	10.0
		2.4
		4.6
		8.4

\* These are published values for the first ionization potential (see ref. 5).

The middle section of Fig. 2 gives three curves obtained with mercury vapor at low pressure and with a small electron current. The negative current is practically negligible as compared with the positive. The upper curves of this figure were obtained with the same electron current but higher pressure and show that the negative ion current starts sharply at the ionization potential. With larger currents and pressures the

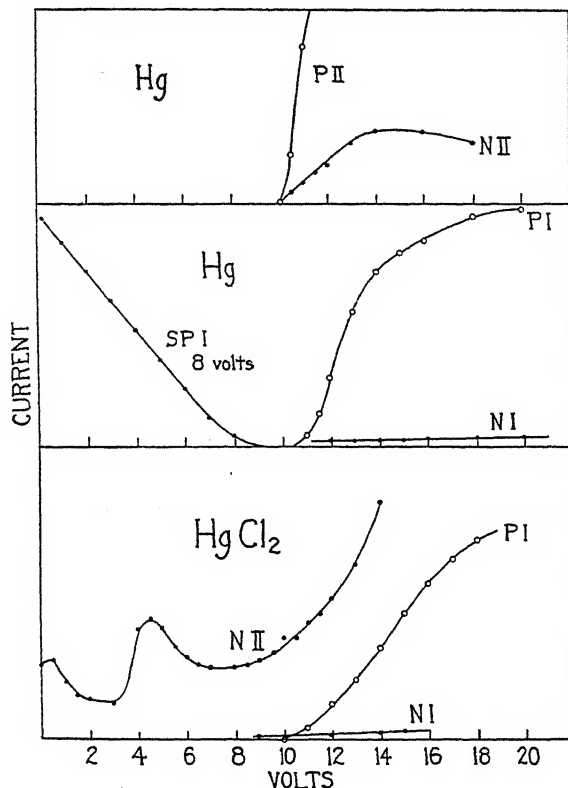


Fig. 2. Ion currents as a function of the potential applied to the electron current. Positive ion curves indicated by  $P$ , negative by  $N$ . Curve  $SP$  shows current against retarding field between  $C$  and  $C'$ .

negative ion currents became nearly equal to the positive but under these conditions the ion currents were far from saturated so that there is no reason to believe that the production of ions was equal.

The lower part of Fig. 2 shows ion currents in  $HgCl_2$  at  $60^\circ C$  (saturation pressure .003 mm). The chloride was partially dissociated upon evaporation as evidenced by the formation of a film of the less volatile mercurous chloride. Curves  $P_I$  and  $N_I$  obtained with low electron current indicate that here too the production of negative ions is small compared with the

amount of positive ions above the ionization potential. However, some negative ions were in this case present at all voltages; curve NII shows on a much larger scale the low voltage portion of a negative ion curve. There is a maximum near zero volts and an increase at an applied potential of about 3 volts (corrected value 4 volts).

Fig. 3 gives current voltage curves in hydrogen chloride. This gas is of particular interest in view of the theoretical considerations mentioned above. The liquid air traps used for freezing out mercury prevented

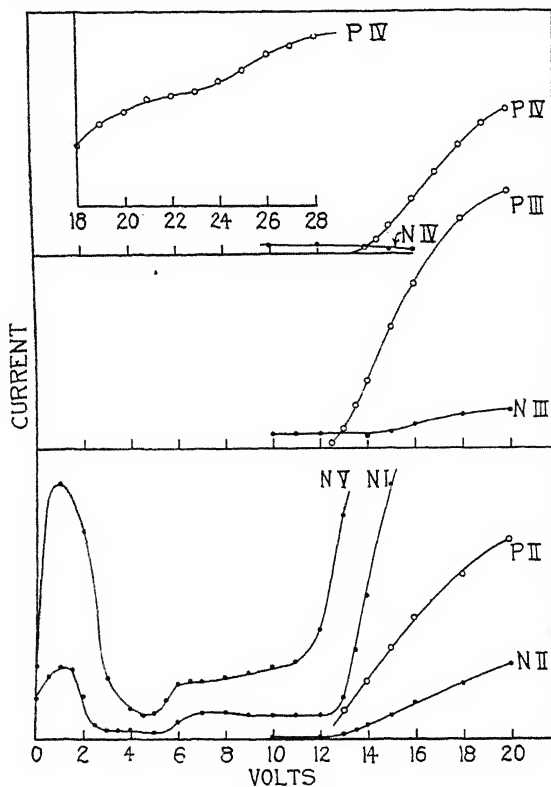


Fig. 3. Positive and negative ion currents in HCl as a function of the applied potential.

the measurement of the pressure under working conditions so that values given in Table II are only rough estimates. Curves PIV, NIV, PIII and NIII, obtained with low pressure and small currents, are, contrary to theory, quite similar to the results obtained in mercury vapor under similar conditions. Above the ionization potential the positive ion current is predominant. The small negative current is, however, measurable at all voltages. The curves in the lower part of the figure were obtained with larger currents and pressures and are similar in general form to those

obtained in  $\text{HgCl}_2$  under like conditions. The ion current *per unit electron current* if plotted would drop sharply from zero volts. There is an increase near 6.5 volts (a large correction has to be added) and another at the first ionization potential. Positive ion currents show a well defined increase at 23.5 volts.

Fig. 4 gives curves obtained with iodine vapor. The upper curves, with the vapor at low pressure, again show the positive ion production pre-

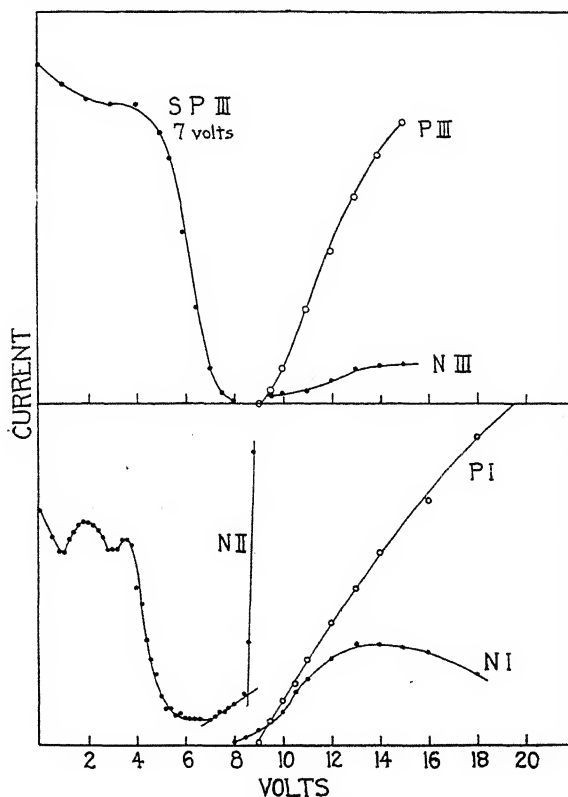


Fig. 4. Positive and negative ion currents in iodine vapor as a function of the applied potential.

dominant. The lower curves taken with much higher pressure show the general features of negative ion curves in the other polyatomic vapors but the critical potentials are in the case of NII exceptionally sharp.

#### INTERPRETATION OF RESULTS

The ion currents above the ionization potential showed the same characteristics in all the gases studied. With low pressures and small electron currents the negative ion currents were negligible compared

with the positive. Increasing the pressure or the electron current made the negative ion current relatively larger and it increased sharply at the ionization potential. The increase with electron current was at first more rapid than the first power of the current (pressure and voltage being constant) while the positive current increase was less than that of the electron current because of departure from saturation.

If polar molecules were ionized into positive and negative ions the results with mercury and iodine should be in marked contrast to those with mercuric chloride and hydrogen chloride. With the latter gases the production of positive and negative ions should be exactly equal. The measured currents would not always be equal as the heavier ions would depart more from saturation, but the two currents would approach equality as the pressure and current were reduced. The observed phenomena are quite different and seem to show conclusively that ionization by dissociation is not the primary effect of the electron collision. The negative ion formation above the ionization potential seems to be a secondary effect depending possibly on the amount of excitation as well as on the current. It is not clear why this secondary effect should start exactly at the ionization potential. The theory of Franck and Grottrian<sup>4</sup> indicates that it would start at some lower critical potential.

All the polyatomic vapors, in contrast to mercury, showed a negative ion current at low voltage. The current dropped rapidly from a maximum at zero volts and increased again at well defined critical potentials. The low voltage current was roughly proportional to the electron current in contrast to the condition above the ionization potential. The critical potentials for iodine were determined with fair precision as 2.4, 4.6, 8.4 and 10.0 volts. Iodine gives potentials of inelastic collision at multiples of 2.3 volts and ionization at 10 volts while there is known to be another excitation stage slightly below 10. These potentials apparently agree with the critical points on the ion curve and suggest a simple hypothesis to account for the form of the curve. Assume that only very slow electrons attach themselves to molecules to form negative ions. Then ions will be formed not only near zero volts but also immediately above potentials of inelastic collision, the function of the collision being merely to reduce the speed of the electron. As the potential is increased beyond the critical value electrons will not lose all their speed and the ion production will again decrease. Conditions are different above the ionization potential for there is reason to believe that slow electrons are produced by ionization even though the voltage is far in excess of the critical potential. Potentials of inelastic collision are not known for HCl and HgCl<sub>2</sub>.

Loeb<sup>10</sup> has shown from analysis of mobility measurements that the probability of electron attachments can be expressed by an equation in which the probability is independent of the electron speed. However, the equation involves the assumption that electron free paths are independent of the speed, which is not strictly true especially at very low speeds. He concludes that the probability of attachment may decrease as the speed increases but that the existence of a "critical potential" for the production of negative ions is excluded. Our results are not inconsistent with this view but many more data are needed before conclusions of any generality can be drawn.

As concerns the process of ionization of polar molecules, while our conclusions are opposed to a commonly accepted theory, they find support in experimental results on positive ray analysis, which show that in general both molecule ions and atom ions are formed in a discharge. J. J. Thompson<sup>11</sup> concludes from data on a great many compounds under different conditions that, with either polar or non-polar molecules, the immediate effect of a collision of a high speed electron is the production of a molecule ion without dissociation. Results with low speed electrons are relatively few and are less conclusive on this point.

Dempster<sup>12</sup> studied ions formed in a thermionic discharge through hydrogen at potentials as low as 90 volts and found that  $H_2^+$  was the primary product of electron collision. Recently Smyth<sup>13</sup> has carried out similar experiments with voltages as low as the ionization potential.<sup>13</sup> Except at very low pressures  $H^+$  and  $H_3^+$  were found, but he gives evidence that they are produced by collisions of  $H_2^+$  with other molecules.

A recent paper<sup>14</sup> on ions formed at low voltage in  $HgCl_2$  and  $HgI_2$  is in apparent contradiction to the present results.  $Cl^-$  and  $I^-$  were found above the first ionization potential, which led them to conclude that the ionization process was of the type  $HgCl_2 \rightarrow HgCl^+ + Cl^-$ . Positive rays from the chloride discharge contained  $HgCl_2^+$ ,  $HgCl^+$ ,  $Hg^+$  and  $Hg^{++}$ . The results are not actually inconsistent with ours for relatively large electron currents are essential in experiments on positive ray analysis and our data show that except with very small currents the production of negative ions is large and increases at the ionization

<sup>10</sup> Loeb, J. Frank. Inst. 197, 45-55 (1924).

<sup>11</sup> J. J. Thompson, "Rays of Positive Electricity," p. 88 *et seq.*

<sup>12</sup> Dempster, Phys. Rev. 8, 651-662 (1916).

<sup>13</sup> Smyth, Phys. Rev. 25, 452-468 (1925). These results indicate that previously published measurements with nitrogen and oxygen as well as hydrogen may have been misinterpreted.

<sup>14</sup> Kondratjeff and Semenov, Zeits. f. Phys. 22, 1-8 (1924).

potential. Thermal dissociation will account for the presence of atomic chlorine and iodine.

A preliminary note<sup>15</sup> on ions formed in HCl gives results which are admittedly inconclusive. At 30 volts  $\text{HCl}^+$  (or  $\text{Cl}^+$ ),  $\text{Cl}_2^+$ ,  $\text{H}^+$  and  $\text{H}_2^+$  are found and with decreasing pressure the hydrogen ions become more prominent. The presence of  $\text{H}_2^+$  indicates that there was molecular hydrogen in the tube and makes the results ambiguous as regards the process of ionization of HCl.

In view of the conclusion that electron collisions do not dissociate molecules in the process of ionization, the agreement shown in Table I between computed and observed ionization potentials is an unexplained coincidence. This work in no way disproves the theory on which the computations are based. The theory gives the work required to separate a positive and negative ion and experiments show that an electron collision is not effective in producing such a separation but simply removes an electron from the molecule. Strangely enough the binding energy of the electron in the molecule is nearly the same as the binding energy of the positive and negative ion in the ideal polar molecule.<sup>16</sup>

BUREAU OF STANDARDS,  
June 11, 1925.

<sup>15</sup> Barton, abstract in Phys. Rev. **25**, 890 (1925).

<sup>16</sup> I have had the privilege of reading proof of a paper by Barker and Duffendack (Phys. Rev. **26**, 339, 1925) which includes spectroscopic observations indicating that in pure HCl there is no radiation in the range of the quartz spectrograph even at 120 volts. They also show that the thermionic discharge gives no dissociation comparable with the thermal dissociation produced by the hot filament. Their conclusions are quite consistent with those here deduced from an entirely different type of experiment.



## ON THE NATURE OF THE IONS FROM HOT PLATINUM

BY HENRY A. ERIKSON

## ABSTRACT

The mobilities of the ions produced by hot platinum were obtained by driving the ions across a stream of air by means of an electric field. The currents at a down stream point were obtained at different values of the field. The current voltage curves for the ions from platinum were compared with curves obtained in a similar manner using ions produced in air by alpha rays. An initial and a final positive ion and one negative ion were found, the same as in the case of the air ions. The mobility values obtained for these ions are also the same as for the air ions. A discussion of the results leads to the conclusion that the negative and final positive ions from platinum are air ions. The initial positive ion may also be an air ion, but this is less certain.

IN an earlier paper<sup>1</sup> results were reported showing that the positive ion from hot platinum has at first a mobility which is the same as the mobility of the negative air ion and the initial<sup>2</sup> positive air ion and that within an interval of the order of 0.3 sec. it changes into an ion which has the same mobility as the final positive air ion. It was also found that if the ions are allowed to remain for a time in the air which has passed the platinum, they load up and form a gradation of larger positive ions.

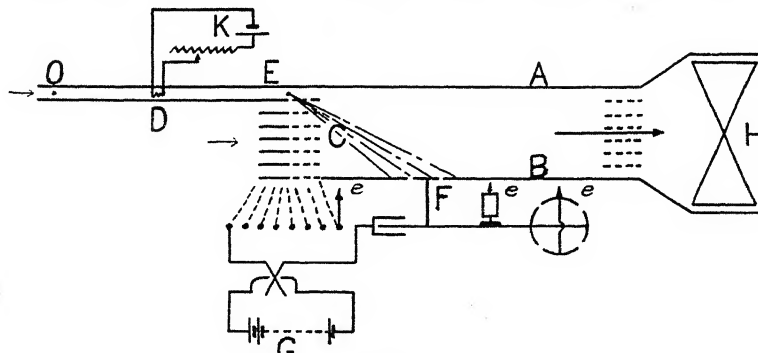


Fig. 1. Apparatus.

As these results were obtained by means of an apparatus which did not have a very high resolving power, it was thought desirable to repeat the work using an apparatus capable of more fully separating the two positive ions.

The method used may be briefly described as follows. By means of a fan *H*, air was drawn between the parallel plates *A* and *B* which were

<sup>1</sup> Erikson, Phys. Rev. **21**, p. 720 (1923).

<sup>2</sup> Erikson, Phys. Rev. **24**, p. 502 (1924).

3.5 cm apart and which were maintained at a difference of potential by means of the battery *G*. The platinum wire was placed at *E*, *D*, or *O*, and was heated by means of a current from the battery *K*. The ions formed at the platinum surface were carried with the air and when in the space between the plates *A* and *B* were drawn to *A* or *B* depending upon the sign of their charges. At plate *B* the current due to the ions coming to a narrow strip *F* was measured. These currents were obtained for different potentials between *A* and *B*. The currents are plotted as ordinates against the potentials as abscissas. By moving the platinum wire towards *O*, the age of the ions was increased. As the ion emission depends upon the length of time the wire has been heated, care was taken to keep the

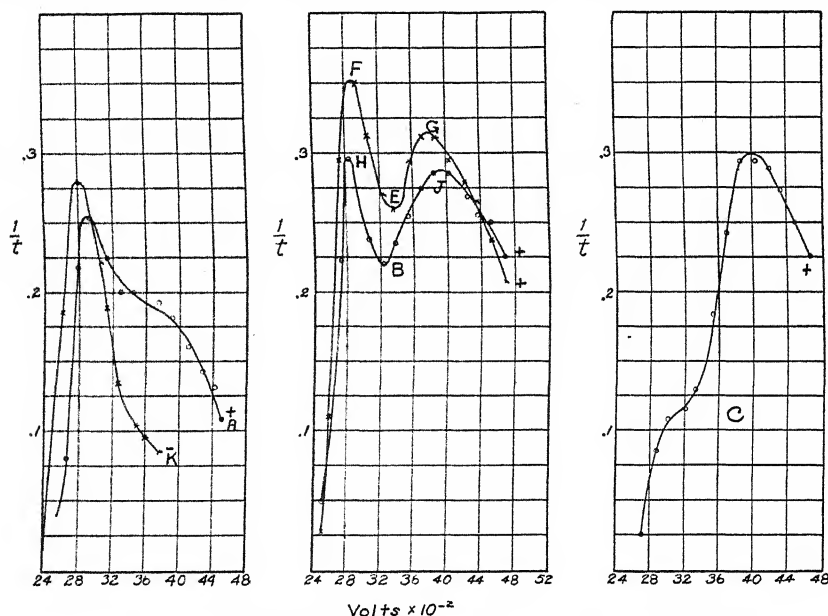


Fig. 2. Currents to strip *F* as a function of potential between *A* and *B*.

heating circuit open between readings. Continuous heating of the platinum during the hour or more required for a set of readings, causes a change in the ion emission which masks, in part, the effect sought for. In the case of the positive ion the platinum was kept at a deep red.

#### THE POSITIVE IONS

The results obtained, in the case of the positive ion, are shown in Fig. 2, where the ordinates represent the currents to the strip *F* in arbitrary units.

Curve HBJ was obtained with the platinum at *D*, Fig. 1, the median position. Curve FEG is for the positive ions produced in air by the alpha

rays from polonium placed at *D*, the conditions otherwise being identical, and is inserted for comparison. The maximum *F* of the air curve FEG is due to the initial positive air ion<sup>2</sup> and the maximum *G* is for the final positive air ion. These correspond respectively to mobilities of 1.87 and 1.36 cm/sec/volt/cm. It is thus seen that hot platinum gives rise to two positive ions which have the same mobilities as the initial and final positive air ions.

That the positive ion from hot platinum which gives rise to the maximum *H* in curve HBJ is an initial ion is shown by the series of curves A, B and C, Fig. 2. The three curves were obtained with the platinum at *E*, *D*, and *O*, Fig. 1, respectively. Comparison of these shows that this ion changes into the slower ion as it becomes older.

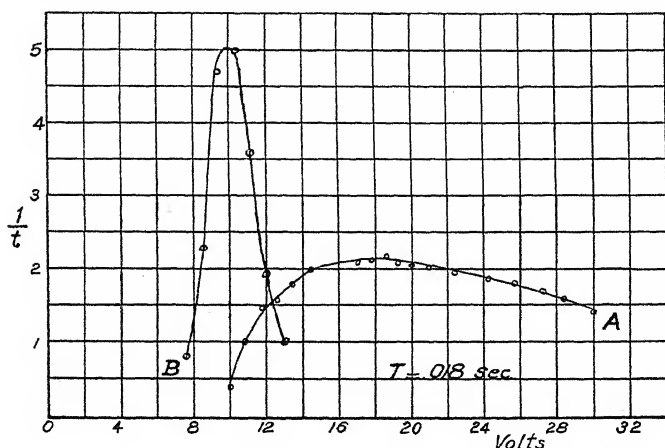


Fig. 3.

In Fig. 3, curve A shows the result when the platinum is placed at *O*, Fig. 1, the velocity of the air reduced, and the platinum raised to white incandescence. It is seen that a gradation of positive ions are obtained. In this case the ions are in an atmosphere of platinum dust for a considerable time and attach themselves to platinum particles of various sizes. Curve B, Fig. 3, is for the negative air ion and shows the position the initial positive ion from platinum would have if present. On account of this loading it is necessary if the pure initial effect is desired, to have the platinum at the lowest temperature which will give sufficient ions for measurement.

#### THE NEGATIVE ION

In Fig. 2, curve K is for the negative ion and was obtained by placing the platinum at *E*, Fig. 1, and heating it to incandescence. Indication of

only one ion was obtained. This ion, it is seen, has the same mobility as the initial positive ion from platinum and hence the same mobility as the negative air ion also.

#### DISCUSSION AS TO THE NATURE OF THE ABOVE IONS

The question as to the nature of the ions from hot platinum can not be completely answered from the standpoint of present experimental evidence. The writer believes, however, that the final of the two positive ions is formed when the initial positive ion attaches itself to a neutral air molecule. That this transition is possible is shown by satisfactory experimental evidence, not only in this but in earlier work on gas ions. It can with fair certainty be said also that the negative ion is an air molecule which has attached an electron since electrons are emitted from hot platinum and such attachments are known to be possible. That the initial positive ion is also an air ion can not be stated with equal certainty, although it is very probable that such is the case, as this ion is not formed continuously in a vacuum. It is difficult to make even a hypothetical statement as to the mechanism of its formation because the electron must pass from an air atom of higher electron affinity to one of lower. Langmuir and Kingdon<sup>3</sup> have shown that caesium atoms upon striking a clean tungsten surface lose valence electrons and leave the surface positively charged. The reason they give for this is that the electron affinity of tungsten is 4.53 volts whereas the electron affinity of caesium is only 3.88 volts and this reason seems entirely valid. In the case in question it is necessary for the electron to pass in the opposite direction. There may, however, be other determining factors. In the case of platinum in air at normal pressure it is one collision in about  $10^{11}$  per sq. cm per sec. with which we are concerned. If metallic conduction is due to free electrons or electron interchange between the atoms of the metal, then some of the platinum atoms it would seem, in view of the thermal agitation, must exist for a time minus an electron. It may be that when a neutral gas molecule collides with one of these positive platinum or metal atoms, it gives up an electron even though its ionizing potential is higher than that of the metal atom.

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PHYSICAL LABORATORY,  
UNIVERSITY OF MINNESOTA,  
February 1, 1925.

<sup>3</sup> Langmuir and Kingdon, *Proc. Royal Society A*107, p. 61 (1925).

## THE MOBILITY OF THE IONS OF THE ACTIVE DEPOSITS OF THORIUM AND RADIUM

BY HENRY A. ERIKSON

## ABSTRACT

The method used is the same as in a similar study of the active deposit of actinium.<sup>1</sup> As in the case of actinium, two positive active bodies differing in mobility were found in the active deposits of thorium and radium. In the case of these three deposits, all of the three swifter bodies have equal mobilities in air, and, likewise, all of the three slower bodies. The curves obtained indicate that one of the active bodies is not deposited as an A product and the other as a B product; nor is one ion atomic and the other polyatomic. It is believed, however, that one is singly and the other doubly charged.

IN an earlier paper<sup>1</sup> results were given showing that in the active deposit of actinium there are two positive bodies, one having a mobility of the order of 4.35 cm/sec/volt/cm and the other a mobility of 1.55.

In this paper are given the results of a similar investigation of the active deposits of thorium and radium. The method employed is similar to that used in the case of actinium.

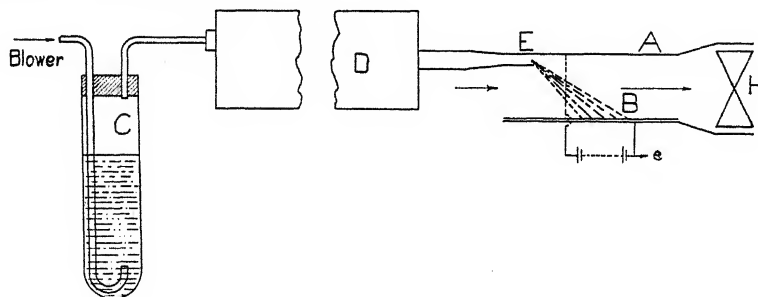


Fig. 1.

The active deposit ions were carried in a stream of air produced by the fan *H*, Fig. 1, and at *E* entered the space between two parallel plates *A* and *B* which were kept at a difference of potential of 3200 volts. The ions were then driven by the field across the air stream to the plate *B* where they were deposited. The plate *B* was removed and placed beneath an ionization chamber in the bottom of which there was a narrow slit, as shown in Fig. 2.

<sup>1</sup> Erikson Phys. Rev. 24, p. 622 (1924).

The rays from the active deposit passing through this slit produced an ionization current which was measured by means of a quadrant electrometer. In this way the down stream position of the different active deposits were located.

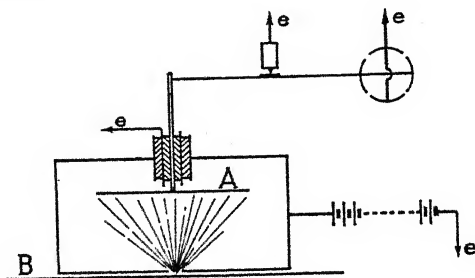


Fig. 2.

#### RESULTS IN THE CASE OF THORIUM ACTIVE DEPOSIT

About 400 gm of thorium nitrate were dissolved in water and placed in a container C, Fig. 1. Air from a blower was forced through the

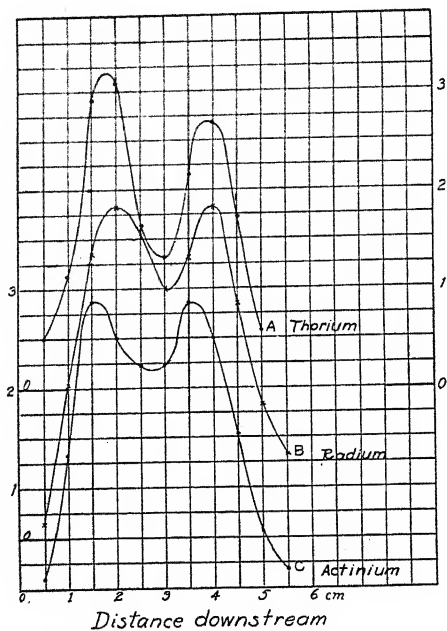


Fig. 3.

solution. The air and emanation then passed into the chamber D, 185 cm long and 36 cm in diameter, so large that the emanation passed through it slowly, thus permitting the formation of a greater amount of active

deposit. From this chamber the active deposit ions passed into the part of the apparatus described above. The time of exposure was one hour, and the air velocity was of the order of 10 meters a second.

The results obtained are given by curve A, Fig. 3, where the downstream distances are plotted as abscissas and the ionization currents as ordinates in arbitrary units. Curve C is for the active deposit of actinium. It is thus seen that there are two active bodies in thorium active deposit and that these have the same mobility as those of the actinium active deposit.

#### RESULTS IN THE CASE OF RADIUM ACTIVE DEPOSIT

The equilibrium quantity of emanation from a solution of about 3 mg of radium was collected in a test tube by displacement of mercury and

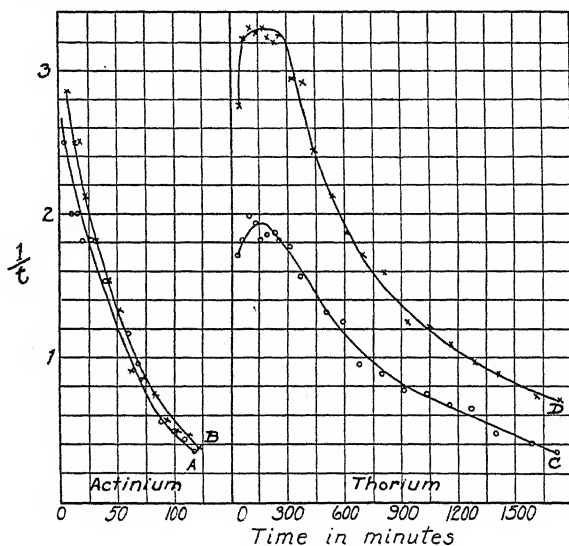


Fig. 4.

was admitted to the chamber D, Fig. 1. A length of exposure sufficient for the chamber to be emptied of the air containing the emanation was used. This interval was of the order of ten minutes. The difference of potential between the plates AB and the air velocity were the same as in the case of thorium. The results are given by curve B, Fig. 3. It is thus seen that in the case of the radium active deposit also there are two positive bodies, the same as in the case of actinium and thorium, and that their mobility values are correspondingly the same.

In Fig. 4 the decay curves for the two bodies in actinium and thorium active deposits are given. Curve A is for the more rapid of the two ions in the case of actinium and curve B is for the slower.



Curves C and D are, correspondingly, the decay curves in the case of thorium.

The half value periods deducible from these curves show that both bodies were B products at time of measurement.

#### DISCUSSION OF RESULTS

In considering the nature of the two bodies, the question arises as to whether originally one came down as an A product and the other as a B product. It is, however, quite clear that this is not the case. If it were so then, owing to the short life of the A product in both the actinium and thorium series, the amount of the A product deposited should be much less. The curves in Fig. 3, however, show that about equal amounts of both are deposited.

It was also thought for a time that one of the active bodies was atomic and the other molecular in size, and that the ion of atomic size, having the greater mobility, would come down sooner. The fact, however, that an ion one atom large has the same mobility in air as an ion one polyatomic molecule large, as shown by the work on argon,<sup>2</sup> precludes this interpretation. The remaining alternative is that one is singly charged and the other doubly charged. An attempt to determine this by means of a magnetic field is under way. Thus far, it has not been found possible to overcome the difficulties encountered.

Financial aid toward this research was given by the Executive Committee of the Graduate School of the University of Minnesota, and the author wishes to express his appreciation of this help.

PHYSICAL LABORATORY,  
UNIVERSITY OF MINNESOTA,  
July 1, 1925.

<sup>2</sup> Erikson, *Phys. Rev.* 25, p. 890 (1925).

## IONIZATION IN REACTING GASES

BY A. KEITH BREWER\*

## ABSTRACT

Ionization associated with the oxidation of ethyl alcohol in contact with electrodes.—Previous work had shown that various gaseous reactions are accompanied by ionization. The oxidation of ethyl alcohol was chosen because of its simplicity. Nitrogen carrying 3 cc of alcohol per minute and also dry oxygen at the rate of 200 cc per minute were sent into a reaction chamber between two concentric cylindrical electrodes. The currents were measured with an electrometer provided with a radioactive shunt. Although potential differences up to 1800 volts (2400 volts per cm) were used, the current was always proportional to the voltage, being evidently far from saturation. The variation with temperature, 150° to 330°C, was exponential, increasing in the case of gold electrodes 20 fold from 200° to 320°C. With Al electrodes the current was only 1/25th as great, and chemical analysis of the products of reaction indicated that the oxidation was also greatly reduced. The results show that the reaction occurs at the electrode surfaces, the rate depending on the material and on the temperature, and that both positive and negative ions are produced. The absence of saturation is probably due to the ions being formed so close to the surface. Copper electrodes gave anomalous results, a negative Cu electrode behaving like Au while a positive Cu electrode behaved like Al. A soft glass electrode behaved like gold, except that the logarithmic increase with temperature was twice as fast for the negative as for the positive electrode.

ALTHOUGH the production of gaseous ionization by means of chemical action has received the attention of a large number of investigators since the time of Lavoisier, the problem is as yet but little understood. Richardson has pointed out the close relationship existing between this chemical effect and the photo-electric and thermionic effects, although the effects in themselves are separate and distinct.<sup>1</sup>

In previous papers<sup>2,3</sup> it has been shown that both endothermic and exothermic gaseous reactions are accompanied by ionization; that the number of ions formed is proportional to the number of molecules reacting, and that the ionic current observed is proportional to the applied voltage over the range investigated.

It is the purpose of the present paper to present evidence which will throw further light upon the production of gaseous ions by purely

\*National Research Fellow.

<sup>1</sup> See "Emission of Electricity from Hot Bodies," by O. W. Richardson for a brief discussion of the history of the subject.

<sup>2</sup> A. K. Brewer and Farrington Daniels, *Trans. Amer. Electrochem. Soc.* **44**, 257 (1923).

<sup>3</sup> A. Keith Brewer, *J. Am. Chem. Soc.* **46**, 1403 (1924).

chemical means. Confusing complications have been reduced to a minimum by confining the study to the oxidation of ethyl alcohol vapor at temperatures well below that of ignition. There appeared to be no accompanying phenomena which could give rise to the ionization observed.

#### APPARATUS

The apparatus used in the present research was similar to that described elsewhere.<sup>2</sup> Several minor improvements were added which made it possible to study the ionization in reactions even at dull red heat, and which increased the sensitivity so that currents as small as  $10^{-15}$  amp. could be read with a reasonable degree of accuracy. The electrometer was of a modified Compton design capable of a sensitivity of over 60,000 mm per volt. The resistance of the radioactive leak, shunted across the electrometer circuit, was  $2.66 \times 10^{11}$  ohms. The gold electrodes were the same as those used in the previous research. Potential was supplied to the electrodes by a bank of Burgess B batteries. A copper-constantan thermocouple, enclosed in a thin walled Pyrex tube, was placed in the reaction chamber in such a manner that the temperature of either the outer, or the inner electrode, or of the reacting gas could be measured.

#### THE REACTION

The ionization was produced by the oxidation of absolute ethyl alcohol at various temperatures below that of ignition. A stream of dry oxygen was admitted to the reaction chamber through one of the inlet tubes, while a stream of nitrogen saturated with alcohol vapor was admitted through the other. The reaction, therefore, took place between the electrodes, and in contact with only the electrodes. The oxygen supply was maintained constant at 200 cc per minute, which was far in excess of that necessary for complete oxidation of the alcohol. The rate of flow of the alcohol vapor was calculated from its vapor pressure to be 3 cc per minute.

#### EXPERIMENTAL PROCEDURE

The ionization which resulted from the oxidation of the alcohol was observed for various electrode potentials, various temperatures of the reacting mixture, and various potential drops between the electrodes. Only one factor was varied at a time in a single set of experiments.

The procedure employed was to adjust the spot of light from the electrometer to a suitable position on the scale by means of the radioactive leak. A supply of oxygen was then admitted to the reaction

chamber through one of the inlet tubes while nitrogen was admitted through the other. No deflection of the electrometer took place. A stop cock was then turned so as to cause the nitrogen to flow through a column of alcohol before entering the reaction chamber. Any ionization that might result from bubbling was removed by passing the vapor through a long tube filled with glass wool, and heated to 200°C. Blank experiments at low temperatures showed the alcohol vapor to be free from any initial ionization. A small induction kick was always noted upon changing the gas entering the reaction chamber; this was readily distinguished from an ionization current.

Upon admitting the alcohol vapor to the reaction chamber a definite deflection of the electrometer was observed, which remained fixed as long as the temperature or the supply of reacting gases was unchanged. When the supply of alcohol was shut off the electrometer returned to the original position. If the supply of oxygen was removed while the flow of alcohol and nitrogen was kept constant, the electrometer never returned quite to the original zero. This was probably due to the fact that the reaction chamber was open at one end so small amounts of oxygen were always present.

The value of the current flowing between the electrodes was calculated by Ohm's law from the known resistance of the radioactive shunt and the voltage as given by the electrometer.

The electrometer was used under both positive and negative control, varying in sensitivity from 6,000 to 36,000 mm per volt. It was found most satisfactory to use positive control and a sensitivity of about 10,000. Since a short electrometer scale was used, the currents observed gave more than full scale deflection for all except the lower applied voltages. For larger currents the electrometer was used as a zero instrument by adjusting the radioactive leak.

#### THE EFFECT OF TEMPERATURE

The effect of temperature on the conductance of the reacting mixture of alcohol and oxygen, between gold electrodes, is shown in Fig. 1. The temperature given is that of the outer electrode, which is higher than that of the gas and the inner electrode. The voltage applied to the outside electrode and the supply of gas were kept constant; the temperature alone was varied. Ionization became detectable at about 150°C, and thereafter increased nearly exponentially with the temperature. For a 10° rise in temperature the conductance increased about 22 percent. The sign of the charge applied to the outer electrode changed only the

direction of the ionic current and did not effect its magnitude or the temperature at which it became detectable.

### THE EFFECT OF VOLTAGE

In Fig. 2 are given the results obtained with gold electrodes, when the supply of reacting gases is maintained constant and the mean potential gradient through the reaction chamber is varied from 0 to  $\pm 2,400$  volts per centimeter. The observed current is directly proportional to the applied voltage, within the limits of experimental error. Although not shown on the curve, the readings were extended down to 2 volts per

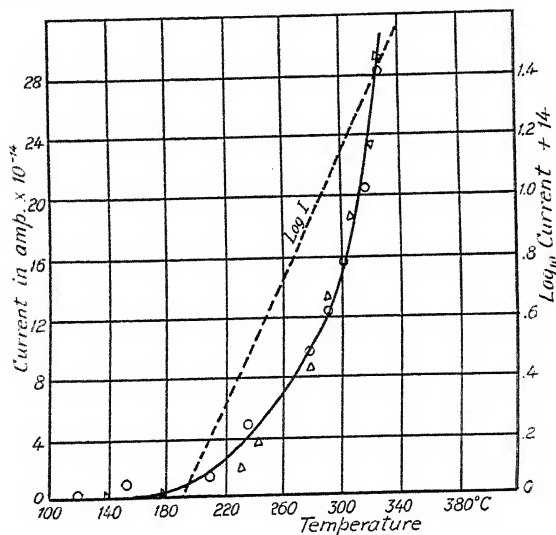


Fig. 1. Potential drop between electrodes 225 volts.  
○ Outer electrode negative. Δ Outer electrode positive.

centimeter potential gradient and the straight line relation was found still to hold. In these experiments the temperature of the reaction chamber was maintained as nearly constant as possible. The temperature of the gas and of the inner electrode was 200°C; that of the outer electrode was 260°C. A slight rise in temperature was always noted during the course of the reaction.

A chemical analysis of the products of the oxidation could not be made satisfactorily. However qualitative tests showed that a small amount of the alcohol was oxidized to aldehyde, to acid, and to carbon dioxide. A quantitative determination was made of the acid.

Since both positive and negative carriers are evidently formed in the reaction in practically equal amounts, it follows at once that the phe-

nomenon is ionic and not electronic. At some point during the course of the reaction the molecules involved must be broken up into positive and negative ions. In this respect the present reaction appears to differ from the reaction studied by Richardson,<sup>4</sup> and by Brotherton.<sup>5</sup> Information regarding the chemical nature of the ions and the conditions necessary for their formation was obtained by changing the material out of which the electrodes were made.

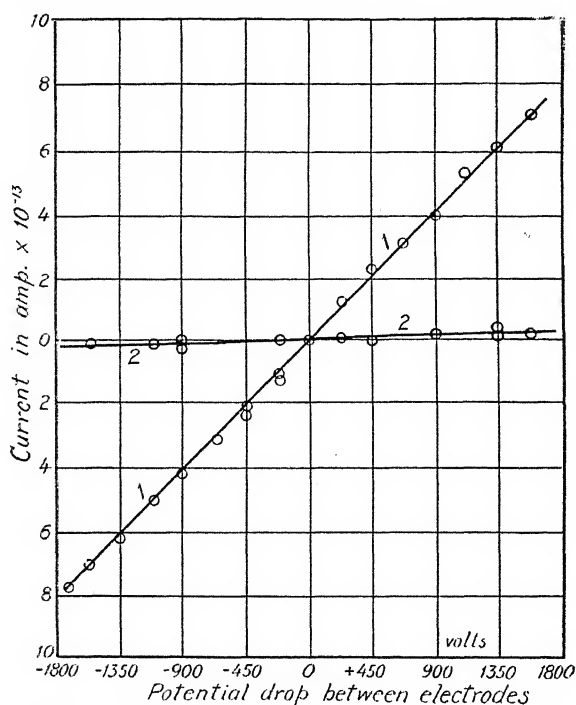


Fig. 2. 1. Gold electrodes; 2. Aluminum electrodes.

#### THE EFFECT OF CHANGING ELECTRODE MATERIAL

Electrodes were constructed of aluminum, of copper, and of soft glass, having the same dimensions as the gold chamber. The glass outer electrode was gold sputtered on the outside to insure better electrical contact with the glass, but the reacting gases, being within the electrode, did not come in contact with the gold film. No difficulty was experienced in using the glass as an electrode for low voltages, because at the temperatures where ionization was detectable the glass was a far better conductor

<sup>4</sup> O. W. Richardson, Phil. Trans. A222, 1 (1921).

<sup>5</sup> M. Brotherton, Roy. Soc. Proc. 105, 468-80 (1924).



than the reacting gas. It was impossible to use the glass at voltages higher than 900 because of electrical leakage from the supports and inlet tubes.

The experiments with the various electrodes were carried out precisely as in the case of the gold chamber. The copper electrodes had to be removed and polished at frequent intervals, because of the formation of a thick film of copper oxide on the surface.

*Aluminum electrodes.* The results obtained with the aluminum electrodes are shown in Fig. 2. It will be noted that for both positive and negative voltages applied the ionic current was very small, varying from 1 to  $5 \times 10^{-15}$  amp. Little if any rise in temperature was noted when the alcohol was admitted to the reaction chamber.

A chemical analysis of the vapors coming from the aluminum chamber showed the absence of a detectable amount of either aldehyde or acid. The aluminum oxide, therefore, does not behave as a catalyst for the oxidation of alcohol vapor.

From these results it follows that in the case of the gold electrodes the ionization observed during the reaction was not produced in the gas filled space between the electrodes but in immediate contact with the gold surface. With the aluminum electrodes the alcohol-oxygen mixture does not come in actual contact with pure metal but instead with a film of aluminum oxide covering the electrode surface. Since this insulating film of oxide is very thin the capacity between the metal on one side and the gas on the other would of necessity be very high, of the order of a farad. Therefore, if the ions were formed in the gas space between the electrodes, irrespective of the material of the electrodes, the electrometer would indicate their presence as well with the aluminum as with the gold. It would appear from this that, for the catalysis of the reaction and the production of ionization, the alcohol and oxygen must be in actual contact with a conducting surface.

The correctness of the above contention was tested by allowing ozone, which is known to decompose in the gas space, to decompose between the aluminum electrodes. An ionic current was observed almost as large as when ozone decomposed between gold electrodes.

*Gold-aluminum electrodes.* Since it has been found that ions are not produced from alcohol oxidation in contact with an aluminum electrode, it becomes possible, by the use of one gold and one aluminum electrode, to tell if positive and negative ions are formed in equal quantities at each electrode, and, in the case of the gold, at which electrode the ions are formed to the greater extent.



The results shown in Fig. 3 (curve 1) were obtained when the outer electrode was gold and the inner electrode aluminum. By comparison with Fig. 2 it will be seen that there is no appreciable difference in the resulting ionization, whether the inner electrode is gold or aluminum.

When the outer electrode was aluminum and the inner electrode gold only a very slight current was observed at the temperature used heretofore. When the temperature of the reaction chamber was raised so that the gold inner electrode came to the temperature of the gold outer electrode in the previous experiment, a current was again obtained about equal to that obtained when the electrodes were used in the reverse order.

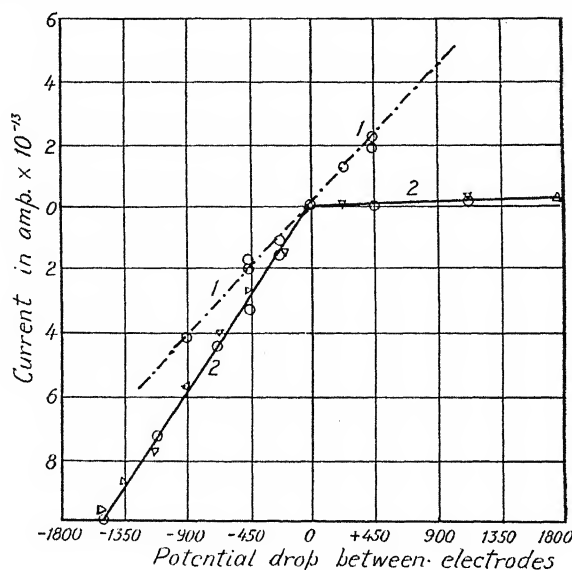


Fig. 3. 1. Gold outside—aluminum inside. 2.  $\circ$  Copper outside and inside;  $\Delta$  Copper outside—gold outside.

From these data the conclusion follows that both positive and negative ions are formed simultaneously on the same metal surface; also that the ions observed in the experiments with the gold electrodes, were formed largely on the outer electrode. The last result was to be expected, since these experiments were conducted at a temperature but slightly above that at which ionization became observable, and since at this particular temperature, there was a temperature difference between the inner and outer electrode of  $60^\circ$ . The fact that similar results were obtained when the inner electrode was raised to the same temperature as the gold outer electrode in the previous experiments is also interesting. Since the radius of the outer electrode is four times that of the inner, the surface exposed to the reacting gas is four times as great. But, since the

electrodes are concentric cylinders, the fall of potential around the inner electrode is four times that around the outer. The similar results, therefore, indicate that the observable ionization is proportional both to the area of the electrode and to the potential gradient at the electrode.

*Copper electrodes.* In Fig. 3 (curve 2) are given the results obtained with copper electrodes. It will be seen that when the outer electrode is charged negatively, the conductance through the reacting gas is but slightly larger than that obtained with the gold electrodes, but when a positive charge was placed on the outer electrode, almost no current was observed. The curve is constructed from data obtained with freshly polished surfaces. When the surface was allowed to coat over with a thick film of oxide the observed current often fell off to a quarter of the above value.

The substitution of gold or aluminum for the inner copper electrode had no appreciable effect on the currents observed. The use of an aluminum outer and a copper inner electrode gave the expected results at elevated temperatures; a current was observed when the aluminum was charged positively but none for the opposite sign.

A chemical analysis of the gases passing through the chamber showed that the quantity of alcohol oxidized fell off rapidly as the copper became coated over with oxide. Satisfactory checks were obtained only with the well coated surface, because the experiment had to be run for about ten minutes to get enough of the reacting products for a chemical test. Under these conditions only about a quarter as many molecules of alcohol were oxidized as in the case of the gold surface. The presence of a field of either sign on the outer electrode made no apparent difference in the number of molecules reacting.

The failure to detect ionization when a positive charge was placed on the outer copper electrode is not understood. It is reasonable to suppose that, since ions were present in all of the previous cases when the alcohol was being oxidized, they were also present in this case but did not become freed from the surface layer in which they were formed.

*Glass-gold electrodes.* In Fig. 4 is shown the current-temperature curve, taken under a potential drop of 300 volts per centimeter, when the outer electrode was glass and the inner electrode was gold. When a positive charge was placed on the glass the ionization curve was almost identical to that obtained with the gold as shown in Fig. 1 except that it began at a slightly higher temperature. For a negative charge on the glass the curve begins at a lower temperature and the logarithmic curve is almost twice as steep.

An accurate current-voltage curve could not be obtained with the glass electrode because of the unsteadiness of the electrometer at high

voltages. From the approximate data, however, it was evident that the straight line relation held as in the previous cases.

The significance of this experiment lies in showing that it is a conducting, and not necessarily a metal, surface that makes possible the escape of ions from the layer of reacting gas.

#### DISCUSSION OF RESULTS

The absence of a saturation current, even at the relatively high voltages used in this research, has a possible explanation in the fact

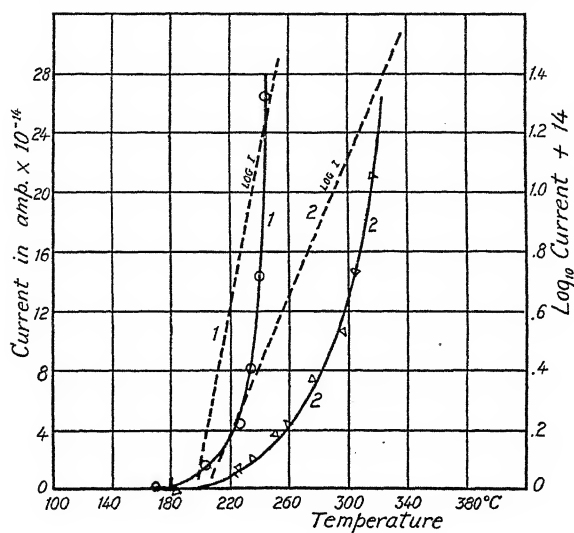


Fig. 4. Potential drop between electrodes 225 volts. 1. Glass electrode negative; 2. Glass electrode positive.

that the source of the ions is in the layer of reacting gases in immediate contact with the electrode surface.

The current observed is constituted by those ions which the field is able to draw away from the reacting layer. However, for the field to draw an ion away from a conductor, it must do so against the electrostatic image of the ion in the conductor. This image force becomes appreciable at a distance of about  $10^{-4}$  cm from the surface. Within this distance the force increases rapidly, i.e., with the inverse square of the distance. Unfortunately, the attractive force cannot be calculated for ions within several molecular diameters of the surface due to the fact that the image forces are overlapped by the stronger molecular forces in the immediate neighborhood of the surface. However, it is reasonable to suppose that an ion at the surface would be held to the surface by a force of several million volts per centimeter.

From the above considerations it becomes apparent that any voltage capable of being used could reach but a short distance into the region in which the image force is appreciable. In fact, only those ions which had moved out to a distance of about  $10^{-3}$  cm from the surface were detected by the highest voltages used in the present research.

If there is a rapid increase in the concentration of ions towards the surface, it would give rise to a straight line relation between current and voltage, with no appearance of saturation. A voltage sufficient to give saturation would be far above that sufficient to cause a spark. Mr. Charles F. Richter has calculated that the concentration of the ions in the layer investigated, increases approximately with the inverse cube of the distance from the surface.

It now becomes possible to suggest an hypothesis for the mechanism of ion formation. A molecule, when driven to the surface of a conductor by kinetic agitation, will be operated on both by the image force of its poles in the conductor, and by the stronger molecular force existing at the surface. (These forces will be entirely independent of any charge placed upon the conductor.) These combined forces will be comparable to the forces holding molecules together. Since the forces acting upon the molecule are electrostatic, the natural consequence is for the molecule to be broken into ions. The ions so formed are then ejected from the surface by kinetic agitation. Ordinarily, the ions, upon being driven from the surface, will recombine to reform the original molecule. Some of the ions, with larger energy content, will be shot out into the fields of other ions, with which they will combine, thus producing chemical reaction. This would explain why only a very small number of the molecules that bombard the surface react chemically.

Mr. Richter has found that if a certain critical velocity of the ions from the surface is necessary for their detection, the variation of the current with the temperature agrees qualitatively with that to be expected from Maxwell's distribution law.

Special acknowledgment is made to Dr. C. F. Burgess, of the Burgess Battery Company, Madison, Wisconsin, for the gift of fifty 45-volt radio B batteries; also to the Department of Physical Chemistry, University of Wisconsin, for the loan of the gold electrodes.

The writer is pleased to take this opportunity to thank Professor R. A. Millikan for his interest in the problem and for his many valuable suggestions.

NORMAN BRIDGE LABORATORY OF PHYSICS,  
CALIFORNIA INSTITUTE OF TECHNOLOGY,  
PASADENA,  
June 15, 1925.

## THE PHOTO-ELECTRIC THRESHOLD FOR MERCURY

By C. B. KAZDA

## ABSTRACT

In order to insure a perfectly clean surface of mercury for test, the apparatus was arranged so that carefully purified mercury flowed intermittently into a shallow iron cup and out through an overflow opening at the surface back into an electrically heated still. Direct observation showed that with such a flow the surface cleans itself of any added contamination very quickly. Also, the results for the wave-length limit were found to be independent of the rate of flow, to a rate far below that normally used, and also unaffected by the presence of gases (air,  $H_2$ ,  $O_2$ , He and  $CO_2$ ) and even of traces of water vapor in the photochamber. The photo-currents to a copper oxide receiver were measured by means of a quadrant electrometer to within about 1 percent for various Hg lines from a Cooper-Hewitt quartz mercury arc, correction being made for stray light by means of intermediate readings. This arc operated at 92-93 volts with 2.1 amp., was constant to 1 percent. Intensity measurements accurate to 1 percent were made by means of a vacuum thermopile connected to a d'Arsonval galvanometer (sensitivity  $10^{-9}$  amp.) using a Hilger monochromator to disperse the light and making correction for stray light by taking readings between the lines. Plots of the ratio of corrected photo-current to corrected light intensity as a function of wave-length give the threshold at 2735Å. The corresponding photo-electric work function is 4.52 volts. This result is free from the objections raised to those of previous observers and seems clearly to be the evaluation of an intrinsic property of mercury uncontaminated by surface impurities.

## INTRODUCTION

FOLLOWING the early phase of discovery by Hertz,<sup>1</sup> Hallwachs,<sup>2</sup> Lenard<sup>3</sup> and J. J. Thomson,<sup>4</sup> later experimentation in the field of photo-electricity has produced a good deal of conflicting evidence regarding the conditions essential to the discharge. While no attempt will be made here to summarize these investigations it may be well, however, to state that they may be divided into two groups. To the first belong those of Fredenhagen,<sup>5</sup> Wiedemann and Hallwachs,<sup>6</sup> Kustner,<sup>7</sup> Hughes,<sup>8</sup> Sende and Simon,<sup>9</sup> and Suhrmann,<sup>10</sup> whose experiments tend

<sup>1</sup> Hertz, *Ann. der Physik*, **31**, 383 (1887).

<sup>2</sup> Hallwachs, *Handbuch der Radiologie* Vol. 3; *Ann. der Physik*, **33**, 301 (1888).

<sup>3</sup> Lenard, *Ann. der Physik* **2**, 359 (1900); **8**, 149 (1902).

<sup>4</sup> J. J. Thomson, *Phil. Mag.* **48**, 547 (1899).

<sup>5</sup> Friedenhausen, *Phys. Zeits.* **15**, 65 (1914).

<sup>6</sup> Wiedemann and Hallwachs, *Ber. Deutsch. Phys. Gesell.* **16**, 107 (1914).

<sup>7</sup> Kustner, *Ann. der Physik* **46**, 893 (1915).

<sup>8</sup> Hughes, *Photo-electricity*, Camb. Univ. Press, 1914 ed.; *Nat. Res. Coun. Bull.* **2**, No. 10 (1921).

<sup>9</sup> Sende and Simon, *Ann. der Physik* **67**, 697 (1921).

<sup>10</sup> Suhrmann, *Ann. der Physik* **67**, 43 (1922).

to throw serious doubt upon the existence of a photo-electric effect which is an intrinsic property of the material under investigation. Most of these workers conclude that the presence of impurities is an essential condition for the appearance of the photo-current. In the second group we have the investigations of Pohl and Pringsheim,<sup>11</sup> Piersol,<sup>12</sup> Millikan and his students,<sup>13</sup> Welo,<sup>14</sup> and Elster and Geitel,<sup>15</sup> who attribute the apparent disappearance of the photo-current to a mere shift in a long wave-length limit as a result of surface impurity. Some investigators (Koppius,<sup>16</sup> Tucker,<sup>17</sup> and others) have shown that the threshold can thus be shifted below the limits accessible to their method of observation.

In 1905 Einstein<sup>18</sup> made the first direct application of the quantum theory to the photo effect and suggested the following well known equation

$$\frac{1}{2}mv^2 = V_e e = h\nu - V_0 e$$

where  $h\nu$  is the energy absorbed by the electron from the light wave,  $V_0 e$  is the work necessary to free the electron from the metal, and  $\frac{1}{2}mv^2$  is the energy of the emitted electron, which is measured by the product of its charge  $e$  and the potential difference  $V$  required to stop it. The validity of this relation between  $V$  and  $\nu$  has been established throughout the range of visible, ultraviolet and x-ray frequencies. The value of  $h$  obtained by Millikan<sup>19</sup> from his photo-electric experiments, is one of the most accurate yet obtained. This equation implies that there is a photo-electric threshold characteristic of the material itself; therefore an important test of the equation is to determine whether or not such an intrinsic photo-electric threshold exists, using an experimental method which is at least free from the objections made to previous experiments.

It was decided to test carefully purified mercury running in a vacuum, for by distillation the mercury can be completely freed from gases and other impurities, and a running surface remains clean. If this should give a definite threshold frequency the matter would be settled.

The method adopted to determine the long wave-length limit was that given by Millikan.<sup>19</sup> The photo-currents per unit intensity were plotted against the wave-lengths used, and the curve extended until it inter-

<sup>11</sup> Pohl and Pringsheim, *Verh. Deutsch. Phys. Gesell.* **16**, 336 (1914).

<sup>12</sup> Piersol, *Phys. Rev.* **8**, 238 (1916).

<sup>13</sup> Millikan and students, see refs. 8, 11, 16, 17, 19, 26, 29.

<sup>14</sup> Welo, *Phys. Rev.* **12**, 251 (1918); *Phil. Mag.* **45**, 593 (1923).

<sup>15</sup> Elster and Geitel, *Ann. der Physik* **48**, 627 (1893); *Phys. Zeits.* **21**, 361 (1920).

<sup>16</sup> Koppius, *Phys. Rev.* **18**, 443 (1921).

<sup>17</sup> Tucker, *Phys. Rev.* **22**, 574 (1923).

<sup>18</sup> Einstein, *Ann. der Physik* **17**, 132 (1905).

<sup>19</sup> Millikan, *Phys. Rev.* **7**, 381 (1916).



cepted the wave-length axis. This involved first the determination of the intensity distribution of the incident light and second the measurement of the photo-current as a function of wave-length.

#### I. MEASUREMENT OF THE ENERGY CONTENT OF ULTRAVIOLET LINES OF THE QUARTZ MERCURY ARC

In order to get sufficient sensitivity for such intensity measurements previous experimenters have used thermopiles in air with Paschen or Thomson Galvanometers. In this work it was decided to use the type of vacuum thermopile employed by Pettit and Nicholson<sup>20</sup> at the Mount Wilson Observatory with a sensitivity 6 to 15 times greater, combined with a high sensitivity d'Arsonval galvanometer obtained from Leeds and Northrup. While the sensitivity ( $10^{-9}$  amp.) is only one tenth that of magnetically shielded galvanometers, the combination of vacuum thermopile and d'Arsonval galvanometer avoided the inevitable fluctua-

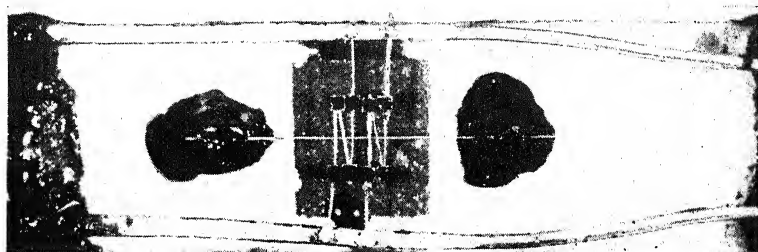


Fig. 1. Photograph of vacuum thermopile used (made by Dr. Pettit).

tions of Thomson galvanometers without loss of sensitivity. It was found necessary to suspend it by a Carman<sup>21</sup> suspension. The telescope was about 3 ft. and the scale about 25 ft. from the galvanometer mirror. This made it unnecessary to estimate the readings to fractions of a millimeter. All of the thermopiles used were made by Dr. Pettit at the Mount Wilson Observatory. (See the article by Pettit and Nicholson for details of construction.) The photograph shown in Fig. 1 is a three fold magnification of the last thermopile used. It will be noted that the thermopile consists of four couples connected in parallel. This thermopile gave exceedingly good results and had a high sensitivity since its resistance was nearly equal to that of the galvanometer. It is mounted upon two platinum leads which are sealed into a glass plug. A glass plate is mounted below with sealing wax and a fine glass tube is fixed upon it, to support the center of the thermopile. Directly below the couples, on the

<sup>20</sup> Pettit and Nicholson, *Astrophysical J.* 56, 295 (1922).

<sup>21</sup> Carman, *J. Opt. Soc. Amer. & R. S. I.* 6, 694 (1922).



glass plate, is placed a piece of fluorescing paper so as to make settings possible in the extreme ultraviolet. The couples were made of bismuth and bismuth plus 5 percent tin, while the receiver was made of tin blackened on the receiving side and placed at the junction. The couples were of the compensated type, and the double deflection was used, thus eliminating the zero reading.

It should be mentioned here that the behavior of thermocouples presumably made in the same way from the same stock of materials is not uniform. Of the considerable number of couples made, some showed drift very badly and were discarded, but those used in this work showed no drift at all and remained useful for long periods of time, reproducing results which checked very well.

As shown in the article of Pettit and Nicholson,<sup>20</sup> the sensitivity of the vacuum thermopile is practically constant for pressures below  $10^{-4}$  mm. The thermopile chamber in our tests was directly connected to a two stage mercury diffusion pump, backed by a Cenco Hyvac pump. There was also a liquid air trap, just beyond the thermopile cell, when the thermopile was in operation. The pressure in the cell as measured by the McLeod gauge, was always less than  $10^{-5}$  mm. The cell was surrounded by cotton to insure uniform temperature on all sides.

The source of light used was a Cooper-Hewitt quartz mercury arc, 100-125 volts d.c., enclosed in an asbestos lined box. The light was resolved by a Hilger monochromatic illuminator, and was then focused upon the thermopile supported inside a chamber which could be evacuated. A special carriage was made for the focusing lens which was provided with two fine screw adjustments by means of which the light could be focused on either one row of junctions or the other. By the use of both of these screw motions, a maximum reading was always obtained for each line. This accounts for the very good agreement of the individual readings obtained.

To insure constancy of operation of the mercury lamp while readings were being taken, it was necessary, in the beginning, to make a careful study of the operating conditions of the lamp. To minimize variations a resistance and reactance were connected in series with the lamp, and a 200 volt storage battery was used as source. It was found that for this lamp, when operated at 92 to 93 volts and 2.1 amp., it was possible to hold the voltage to within one volt. It might be mentioned here that it took about one hour for the lamp to reach these best conditions of operation after starting up.

The slit width used in all measurements of intensity was 20 divisions (0.5 mm) on the slit screw head of the Hilger Monochromator. Tucker<sup>17</sup>

made a measurement of the intensity for the same lines, but used a slit width of 25 divisions. The stray light which appears as a general background on photographic spectrum plates gave a measurable thermopile deflection. In general the minimum reading between two lines was taken as measuring stray light, except in the case of 2620 where weak lines were present (see Table I). The corrected value for the intensity for a given line was obtained by subtracting the nearest interpolated value for stray light from the observed intensity reading. The method is limited by the necessity for this correction which below 2300A becomes very large,<sup>22</sup> as well as by the fact that at 1900A we begin to get strong absorption by air and quartz.

TABLE I

*Typical set of readings of intensity of mercury lines from quartz arc.*

Wave-lengths Lines	Background	Readings in mm					Average	Correction for stray	Corrected average
	2840A	14	14	14	14	14	14		
2804A		142	144	146	144	144		16	128
2754		43	45	44	44	44		21	23
	2725	22	23	21	22	22			
2700		56	55	56	56	56		22	34
2653		274	274	277	280	277		21	255
	(2620)	33	34	33	34	(33.5)			
2537		370	369	368	367	368		20	348
	2505	19	19	20	20	19.5			
2483		95	98	97	98	97		18	79
	2435	16	15	16	16	16			

Table I gives a representative set of readings and indicates how closely the individual readings agree. This table covers only the region of wave-lengths used in the photo-electric investigation described below. It will be noticed that down to 2483A the deviation from the average is less than 3 percent and in some other measurements, not here given, the agreement was even better.

Table II gives the average values of the deflections for three other sets of readings. These sets of readings were all taken under the same experimental conditions, the voltage across the lamp being 92 to 93 volts and the current 2.1 amp. The lamp could have run at higher temperatures to get greater intensity but the precautions that would have been necessary were not warranted since sufficiently large readings were obtained for this region of wave-lengths.

While the readings did change from time to time, it was found that over the intervals of time used in the latter part of the investigation, the readings remained practically constant. Readings taken one set after

<sup>22</sup> Souder, Phys. Rev. 8, 310 (1916).

another, during the same afternoon, changed hardly at all. Over thirty sets of readings were taken.

## II. DETERMINATION OF THE PHOTO-ELECTRIC LONG WAVE-LENGTH LIMIT FOR A CLEAN SURFACE OF LIQUID MERCURY

Extreme care was taken to obtain pure mercury. The occluded gases were completely removed by repeated distillation in an atmosphere of mercury vapor, and the photo-current was measured as soon as the fresh surface was presented to the vacuum chamber. In this way two important objections to previous experiments are removed.

TABLE II

*Three sets of average readings for intensity of mercury lines*

Wave-lengths	Uncorrected			Corrected		
	9/8/23	9/12/23	9/15/23	9/8/23	9/12/23	9/15/23
2804A	146 mm	144 mm	147 mm	133 mm	130 mm	130 mm
2754	45	44	46	23	22	23
2700	56	54	55	34	33	34
2653	280	276	283	257	255	260
2537	370	369	368	350	350	348
2483	97	97	97	82	80	81

After being put through the wet process, the mercury was purified by the method given by Hewlett and Minchin<sup>23</sup> which is the same as that used by Harkins<sup>24</sup> in preparing mercury for use in isotope determinations. This method consists in evaporating mercury while bubbling air through it. The mercury was then placed in a still directly connected with the photo-electric chamber. All the apparatus had previously been carefully cleaned, washed and dried and then heated for some time while being evacuated before the mercury was finally inserted. This still was made of Pyrex glass shaped like one stage of an ordinary diffusion pump, as shown in the diagrammatic sketch (Fig. 2). The still was provided with an electric heater of which the current could be varied by external resistance to regulate the rate of evaporation. The process was carried on at low pressures since the still was directly connected to the vacuum pumps.

Continuously overflowing mercury was tried, but it was observed that the center of the surface remained stationary, while the mercury flowed out at the groove from underneath. Intermittent flow, however, was found to be effective in keeping the surface clean. Rough experiments with mercury in a glass cup with a V groove in it, showed that after a

<sup>23</sup> Hewlett and Minchin, *Phys. Rev.* **21**, 388 (1905).

<sup>24</sup> Harkins and Mulliken, *Jour. Amer. Chem. Soc.* **44**, 37 (1922).

few overflowings, even the trace of oil which had been dropped on the surface could not be distinguished with a strong magnifying glass (and later a microscope). Fine dust could be observed to be drawn out through the groove from all parts of the surface. Thus intermittent overflow is a definite means for the removal of surface films which might possibly form when the surface is exposed to the chamber probably because the surface film is broken each time an overflow takes place. Intermittent overflow was automatically produced by the mercury dropping from the condenser. From the overflow the mercury returned to the still and was

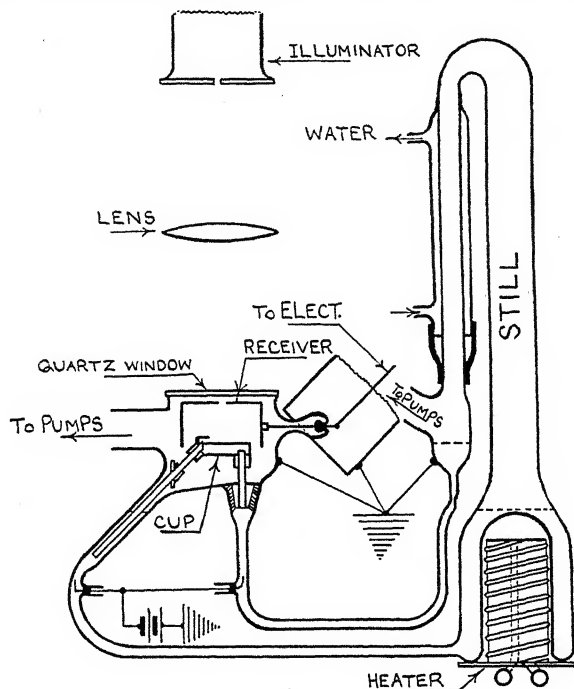


Fig. 2. Apparatus, including cup with mercury surface cleaned by intermittent overflow.

re-evaporated again. The cup itself was shallow so that a given molecule of mercury could not remain at the surface exposed to the vacuum chamber more than a second.

The attempt to take electrometer readings with overflowing mercury has been made before by McGougan<sup>25</sup> in connection with delta rays produced by alpha rays. Others have tried it also without success. I encountered the same difficulty as they did at first, namely, an erratic behavior of the electrometer as soon as the overflow commenced. A glass cup and vertical outlet tube was being used, and the trouble seemed to be caused by friction on the glass and by separation of the mercury into

<sup>25</sup> McGougan, Phys. Rev. 12, 122 (1918).

drops. Therefore, a change was made to the iron cup and the outlet tube of iron placed at 45 degrees. The inlet tube of iron was fitted into a ground joint in the chamber, and cemented with a special high temperature cement kindly furnished by the Mantle Lamp Company of America. (This cement was also used to attach the quartz window.) While the trouble was not eliminated, it was decreased considerably. A further search was made and at last it was found that the main source of trouble was in the mercury condensation tube since a large static charge is produced when the mercury strikes the walls of the tube. So the whole condensation tube and photo chamber were closely wrapped externally by tin foil which was then grounded. The erratic behavior of the electrometer ceased entirely and results followed quickly.

The vacuum pumps were directly connected to the photo chamber and run continuously during the experiment. The pressure was read by a McLeod gauge and was never more than  $10^{-5}$  mm. This does not include the pressure of the mercury vapor which was of the order of  $10^{-3}$  mm at room temperature. A liquid air trap was situated near the photo chamber. Air was never introduced except through a number of drying tubes of calcium chloride and phosphorous pentoxide.

As shown in the diagram, the cup is surrounded by a copper oxide receiver. A slit in the top permits the illumination to reach the mercury in the cup. The slit is of such dimensions as not to be touched by the concentrated light from the illuminator. The same condensing lens was used as in the intensity measurements. The thermopile chamber and the photo chamber were side by side and the lateral screw motion on the holder of the condensing lens was large enough to enable the light to be focused on either chamber.

The monochromatic illuminator was mounted so that both collimator and telescope were in the same vertical plane. The lamp was mounted on a special carriage and rigidly connected to the illuminator, so that the light could be shifted from one chamber to the other by motion along a guide. This moving element being heavy was counterweighted from the ceiling so that the shift could be made easily and quickly.

The photo-current readings were made with a Cambridge and Paul Dolezalek quadrant electrometer. One pair of quadrants was grounded while the other pair was connected to the receiver. The sensitivity was 1250 mm per volt with the scale at 150 cm distance for a needle voltage of 92. The photo surface was kept sufficiently negative to ground to insure maximum readings.

The electrometer readings were taken for periods of 40 seconds or more for small currents and 8 seconds for large currents, but were all



reduced to an 8 second basis. The time interval was measured by means of a metronome which was frequently checked against a stop watch and was controlled by means of a camera shutter fitted to the outlet hole in the box containing the mercury lamp, between it and the illuminator. Correction for the electrometer leak, which was always very small and taken with each observation, was always applied to the reading. The minimum readings between lines were taken as in the intensity measurements and the same procedure was followed in correcting for stray light. This is very important here for the stray light may be composed of wave-lengths above and below that of the line itself.

As the heater on the mercury still was started at the same time as the lamp, the mercury was evaporating for some time before readings were begun. A set of intensity readings for the various wave-lengths was taken first, followed by a set of photo-current readings. Care was taken to get a maximum for each reading and three or four readings were taken for each line.

#### EXPERIMENTAL RESULTS

Table III gives a representative set of detailed photo-current readings. The maximum deviation from average in Table III is less than 3 percent. Thus the accuracy of measurement of the photo-current is about the same as that of the light intensity.

TABLE III

Wave-lengths Lines	Bet. lines	Time (sec.)	Reading in mm				Stray*	Correct.* av.
			1	2	3	Aver.		
2804A		240	0	0	0	0	0	0
	2770A	80	0	0	0	0	0	.....
2754		80	10	10	10	1.0*	1.0	0
	2725	40	17	17	16	3.6*	3.6	.....
2700		8	12	12	12	12.0	6.2	5.8
2653		8	129	125	128	127.0	18.0	109.0
	(2620)	8	38	38	38	(38.0)		
2537		8	444	465	461	456.7	32.0	424.7
	2505	8	32	33	32	32.3	32.3	
2483		8	166	167	164	165.7	32.0	133.7
	2435	8	31	30	31	30.7	30.7	

\* Reduced to a time interval of 8 sec.

No mention is made by most investigators of stray light corrections to their readings but to show the magnitude of this correction, the values are here given for both the corrected and uncorrected readings. Table IV gives the photo-current readings corresponding to the intensity measurements in Table II. The thirty sets of readings which were taken all closely check with these three sets.

In every case, a deflection was obtained for 2700A but none whatever for the much more intense line 2804A, even when exposed for several minutes. In the case of 2754A, the very small deflection obtained over a period of 40 sec. was just equal to the deflection given by the stray light for that line, so its net reading was zero. These readings were the same even when the rate of overflow was decreased somewhat. It seems certain, therefore, that the surface could not be contaminated in any way by this extremely short contact with the vacuum chamber.

TABLE IV

Wave-lengths	Uncorrected			Corrected		
	9/8/23	9/12/23	9/15/23	9/8/23	9/12/23	9/15/23
2804A	0 mm	0 mm	0 mm	0 mm	0 mm	0 mm
2754	0.8	0.7	1.0	0	0	0
2700	12.5	12.0	12.0	5.2	5.5	5.8
2652	128.0	126.0	127.0	109.0	108.0	109.0
2537	451.0	450.5	456.7	420.0	425.0	424.7
2483	165.0	164.0	165.7	135.0	132.5	133.7

As a further test, air, hydrogen, oxygen, helium and carbon dioxide were introduced into the chamber. No extended effort was made to purify them but they were very carefully dried beforehand. Under the conditions of this method *with a rapidly changing surface they were without effect upon the limit*. Even a trace of water vapor at rapid intermittent flow was without effect. These results could be reproduced at will.

As mentioned before, the long wave-length limit or threshold is obtained by plotting the photo-current per unit intensity against the wave-length or frequency, and extrapolating the curve to the intersection with the latter axis. Since the strong line 2804A gives no deflection and the much weaker line 2700A (see Table I) gives a good deflection, it is certain that the limit must fall between them.

It must be borne in mind that this intersection is governed by the points near the axis and not at all by points farther away from the axis, and therefore, it is useless to make measurements far from the axis. The curves were drawn on a large sheet of cross-section paper 20 inches wide and 40 inches long and use was made of regulation draftsmen's long flexible guides and weights and the natural position of the guides in every case governed the direction. This insures a uniform method of drawing the curves because the guides are in contact with the paper at only a few places so that the friction of the guides with the paper is small.

Since the individual curves all fall very close together, in Fig. 3 are given only the curves obtained by plotting the ratio of the final average



values of the photo-current readings and of the corresponding intensity readings, both uncorrected and corrected, against the wave-length. The individual curves, on a large scale, show a variation of plus or minus 10A for the threshold value, for both corrected and uncorrected. It will be observed that the photo-current, due to stray light, decreases rapidly as the wave-length increases beyond 2750A dropping to zero at 2770A. while the intensity reading (Table I) is still 144 mm at 2804A. This indicates that, fortunately, the stray light here is largely of longer wave-length and hence does not excite photo-emission. As a result the average curve for the uncorrected effect gives practically the same threshold value

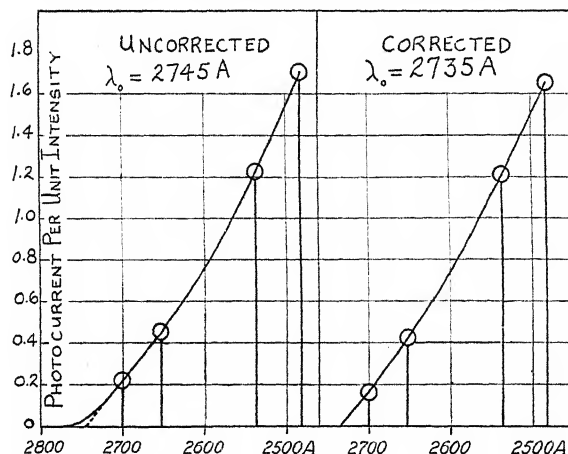


Fig. 3. Photo-current from clean mercury surface as a function of wave-length, corrected for stray light and uncorrected. Value for 2754, uncorrected, is .019.

(2745A) as the average curve for the corrected effect. Nevertheless, as emphasized by Professor Millikan,<sup>19</sup> to determine the threshold accurately it is important to make the correction for stray light.

#### DISCUSSION

The only other data that could be found for mercury were some given by Derieux<sup>26</sup> and a curve by Pringsheim. Derieux states that "the drops of mercury were sensitive to line 2536A but not to line 3126A and the lines between were too weak to give any readings." The curve by Pohl and Pringsheim is given on page 76 of Hughes' book on photo-electricity. The last reading is for line 2536A. Klages<sup>27</sup> made an attempt to work on mercury in 1909 but does not mention the limit.

<sup>26</sup> Derieux, Phys. Rev. **11**, 276 (1918).

<sup>27</sup> Klages, Ann. der Physik **31**, 343 (1910).

Tests with water vapor showed that it has a marked effect upon *stationary mercury* even though present in extremely small amounts. The effect of a trace of water vapor at  $10^{-5}$  mm pressure was very noticeable. *It raised the long wave-length limit. When a greater amount of water vapor was admitted the limit was pushed below the lowest value the apparatus was capable of measuring.* That a film of water vapor can exist on mercury and have a noticeable effect has also been found by Iredale<sup>28</sup> in connection with surface tension measurements at pressures of the order of  $10^{-5}$  mm.

It is entirely possible that water vapor is responsible for much of the non-agreement in previous work in this field. It was also found that when once admitted water vapor is extremely hard to get rid of. However, in this experiment, as stated above, the presence of a trace of water vapor did not affect the readings *when the surface was changing rapidly.*

It seems clear that the present method for determining the threshold value for mercury is free from the chances of contamination present in previous experiments. The measurement of photocurrent at the instant a clean photosurface is presented, has not been tried before.

Millikan<sup>29</sup> has pointed out that the necessary conclusion from the constancy of stopping potentials is that each metal has a definite long wave-length limit and that furthermore, the photo-electric and thermionic work required to remove an electron from the surface should agree. The value of the photo-electric work function computed from the measured long wave-length limit is

$$h\nu_0 = 300 hc/e\lambda_0 \times 10^{-8} = 12345/\lambda_0 = 4.52 \text{ volts}$$

assuming  $e = 4.77 \times 10^{-10}$ ;  $h = 6.55 \times 10^{-27}$ ;  $c = 3 \times 10^{10}$ ;  $\lambda_0 = 2735 \text{ \AA}$ .

In conclusion, I wish to thank Professor Millikan for suggesting this work with flowing mercury and for putting the facilities of the laboratory at my disposal.

NORMAN BRIDGE LABORATORY OF PHYSICS,  
CALIFORNIA INSTITUTE OF TECHNOLOGY,  
PASADENA, CALIFORNIA,  
November 20, 1923\*

<sup>28</sup> Iredale, Phil. Mag. 45, 1088 (1923); 48, 177 (1924).

<sup>29</sup> Millikan, Phys. Rev. 18, 236 (1921).

\* Received Jan. 20, 1925; revised Aug. 20, 1925.—Ed.

## THE VARIATION IN THE PHOTO-ELECTRIC EMISSION FROM PLATINUM

BY ALBERT E. WOODRUFF

## ABSTRACT

**Photo-electric emission from Pt.**—The specimens were ribbons 3 cm by 5 mm by .013 mm thick, mounted in a Pyrex tube with a quartz window. *Effect of heat treatment on sensitivity.* Fresh specimens, cleaned with nitric acid, were insensitive to mercury arc radiation, but became sensitive when heated to moderate temperatures (250°C) by means of an electric current through them, though heating to a much higher temperature in an electric oven was without effect. Prolonged heating (17 hr) at 1300°K with pressure of  $10^{-6}$  mm, reduces the sensitivity to light transmitted by quartz to zero. One specimen so treated remained inactive for 2 months. With pressures below  $10^{-7}$  mm the sensitivity begins to return as soon as heating is stopped, the rate of recovery depending on the wave-length, the pressure and the previous treatment. A specimen insensitive to mercury arc radiation, was sensitive to the radiation from a tungsten filament within the tube, showing that the insensitivity is due to a shift of the threshold to short wave-lengths. *Thermionic measurements* gave an increased value for the work function  $\phi$  when the threshold  $\lambda_0$  was shifted to wave-lengths below that transmitted by quartz, in general agreement with the theoretical relation between  $\phi$  and  $\lambda_0$ . At low pressures, a change of sensitivity in the ratio 1 to 7 was observed without a shift of the threshold wave-length. *Effect of electric field.* After prolonged heating at  $10^{-6}$  mm, small electric potentials, 0.01 to 0.06 volt, are sufficient to prevent the escape of all electrons excited by mercury arc radiation. If the pressure is much lower the electric field shifts the long wave-length limit toward shorter wave-lengths. In both cases photo-activity is not restored when the retarding field is removed but only when an accelerating field is applied. The effect appears to be instantaneous. These results seem to require an adsorbed layer of gas for their explanation. However, the layer formed by heating at high temperatures seems different from that initially present in fresh specimens. This seems to be a retarding ionic layer formed from the residual gas, since at the lowest pressures this seemed to cover only patches of the surface.

**Photo-electric measurements with an iron arc**, in spite of fluctuations, were made possible by balancing the current against that from a standard cell illuminated by a fraction of the same light by means of a rotating prism and a variable rotating sector.

## INTRODUCTION

FOR the relation of the energy of an electron emitted photo-electrically to the frequency of the incident light, Einstein has proposed the equation

$$\frac{1}{2}mv^2 = Ve = h\nu - w_0.$$

In this equation  $w_0$  is assumed to be constant for a given substance and equal to  $h\nu_0$ ,  $\nu_0$  being the lowest frequency of radiation that is capable of

ejecting an electron. Numerous attempts have been made to check this equation experimentally and to find  $\nu_0$  for the various substances. The experiments of Millikan and others,<sup>1</sup> particularly with the alkali metals, have furnished for a number of substances a value of  $\nu_0$  which appears to be characteristic of the substance. The experiments with platinum have not been so successful. Among the values first given for the long wave-length limit  $\lambda_0$  for platinum corresponding to  $\nu_0$  is that obtained by Richardson and Compton:<sup>2</sup> viz., 2880Å. Later Koppius<sup>3</sup> reduced this value to 2570Å. He obtained the lower value simply by baking his apparatus to get rid of gases and by heating his platinum specimens. Two years later, Tucker<sup>4</sup> by still more severe methods of ridding his platinum specimens of gas, was able to reduce  $\lambda_0$ , temporarily, to a value below the shortest wave-length transmitted by quartz.

Wiedmann and Hallwachs and their students<sup>5</sup> working in the Physical Institute, conclude from their experiments with platinum that its photo-activity must be due almost entirely to absorbed gases and that a gas free specimen of platinum would show practically no photo-activity if excited by radiation of wave-length ordinarily used. They conclude that the action of gas upon the discharge of photo-electrons from a metal should be of two kinds; (1) an adsorbed layer of gas on the surface hinders the discharge of photo-electrons, and (2) gas absorbed in the metal assists in the process of discharge of photo-electrons. Indeed, Simon thinks that at least 99.9 percent of the photo-electrons from platinum, obtained by illumination with a quartz mercury lamp, are emitted with the assistance of absorbed gases. Hence if it were not for gases platinum would be photo-electrically inactive. According to this theory, when a metal is heated and the surface film driven off the photo-electric current should increase because the retarding influence of the surface film is removed; while more intensive heating, sufficient to drive out the absorbed gas, should reduce the photo-electric current.

A second consequence of this theory would be that the long wave-length limit should be shifted toward longer wave-lengths by the initial outgassing because of the removal of the surface layer which retards the slow moving electrons. Further outgassing, which removes the absorbed

<sup>1</sup> R. A. Millikan, *Phys. Rev.* **7**, 18 (1916); Hennings and Kadesh, *Phys. Rev.* **8**, 209 and 221 (1916); Sabine, *Phys. Rev.* **9**, 210 (1917).

<sup>2</sup> Richardson and Compton, *Phil. Mag.* **24**, 575 (1912).

<sup>3</sup> Koppius, *Phys. Rev.* **18**, 443 (1921).

<sup>4</sup> Tucker, *Phys. Rev.* **22**, 574 (1923).

<sup>5</sup> Wiedmann and Hallwachs, *Deutsch. Phys. Ges.* **16**, 107 (1914); Kober and Hallwachs, *Phys. Zeits.* **16**, 95 (1915); Stumpf, *Deutsch. Phys. Ges.* **16**, 989 (1914); Sende and Simon, *Phys. Zeits.* **21**, 562 (1920).

gases, should cause a return of the long wave-length limit to smaller values because the assistance of the forces of the absorbed gases is no longer present.

Suhrmann,<sup>6</sup> working in the laboratory mentioned above, attempted to demonstrate the truth of this theory. He tested the theory in two series of experiments, not only for photo-electric discharge of electrons but also for thermionic discharge of electrons. He used platinum and tantalum in his tests, the results of his investigations being about the same for both metals.

For platinum Suhrmann found that the long wave-length limit shifted from 2600Å to 3000Å and back again to 2600Å as the outgassing process continued. He found that the photo-electric current excited by the wave-length 2650Å decreased to a value which was only 0.17 percent of the maximum value excited by this wave-length; that excited by 2170Å fell to 13.5 percent of the maximum value. Likewise the thermionic current decreased with outgassing. The value of  $\phi$  in the Richardson equation was found to be 4.569 volts from the thermionic data for the outgassed condition, as compared with 4.57 volts calculated from the long wave-length limit measured at the same time that the thermionic data were taken. But the values of  $\phi$  found by the two methods did not agree for the slightly outgassed condition. The value of  $\phi$  corresponding to 3000Å is 4.11 volts while the smallest value of  $\phi$  from thermionic data is the value 4.569 volts. To account for this discrepancy Suhrmann assumes that photo-electrons come from the free electrons and that the decrease of photo-emission is determined more by the number of free electrons in the metal than by the work required to get an electron through the surface. His thermionic measurements show that the value of  $A$  in the Richardson equation, which is proportional to the number of free electrons, decreases from  $4.76 \times 10^{27}$  for the slightly outgassed condition to  $1.7 \times 10^{26}$  for continued outgassing. Suhrmann thinks that these results of his investigation confirm the theory of Wiedmann and Hallwachs.

Although the work of Suhrmann appears to confirm this theory in many respects, yet there are important experimental facts for which the theory does not account. These will be discussed later. Suhrmann's proof of the theory is based upon the assumption that photo-electrons come from free electrons. This assumption is contrary to our interpretation of the facts that photo-electric velocities are independent of temperature and that insulators are photo-active. Furthermore, the Compton effect,<sup>7</sup> which has been experimentally demonstrated, leaves little

<sup>6</sup> Suhrmann, *Ann. der Phys.* **67**, 43 (1922); *Zeit. f. Phys.* **13**, 17 (1923).

<sup>7</sup> A. H. Compton, *Phys. Rev.* **21**, 483 and 715 (1923); **22**, 409 (1923);

P. A. Ross, *Proc. Nat. Acad.* **7**, 245 (1923); Becker et al., *Phys. Rev.* **23**, 763 (1924).

room for doubt that photo-electrons come from bound electrons. Suhrmann is led to make his assumption partly on account of the fact that a change in the value of  $\phi$  of only 0.46 volt is not sufficient to account for the very great decrease in the photo-electric current that occurs as the metal is freed from its absorbed gas. Yet when the surface layer of gas is removed from a fresh specimen the increase in the photo-electric current is greater than the decrease from the maximum value as the specimen is outgassed. But the change in the long wave-length limit during the increase is not greater than it is during the decrease in the photo-electric current. Granting that the change in  $\phi$  is not sufficient to account for the change in the photo-electric currents, how is this change brought about in the case of an increase when the absorbed gas is present? Suhrmann carried out his experiments under certain conditions and obtained these

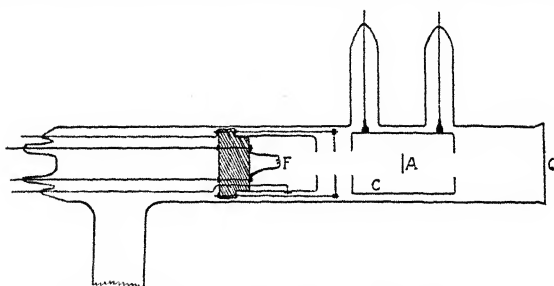


Fig. 1. Diagram of photo-electric tube.

results. Only a slight variation of the conditions would have given him quite different results. It is the purpose of the investigation reported in this paper to give results made under various conditions.

#### EXPERIMENTAL ARRANGEMENT

A photo-electric cell was made from a 40 mm Pyrex tube from which all wax and ground joints were eliminated in order to make it possible to obtain a very high vacuum. A quartz window *Q* (see Fig. 1) was sealed to one end of the tube with a graded seal made by the Cooper-Hewitt Electric Company. The platinum specimens *A*, which were ribbons 3 cm long, 0.5 cm wide, and 0.0013 cm thick, were mounted on tungsten rods sealed into glass side tubes. A copper oxide cylinder *C*, completely surrounded the specimen except for a hole in each end of the cylinder which allowed the incident energy to pass. The whole tube could be enclosed in an oven and baked. Mercury vapor was kept out from the experimental chamber by a liquid air trap located just outside the oven. The platinum foil could be heated by an electric current through it. The diagram shows the arrangement of the tube.



Photo-electric currents were measured with a Dolezalek electrometer which could be brought to a sensitivity of 3000 divisions per volt, if desired. Thermionic currents were measured with the electrometer or with a galvanometer. A Hilger illuminator was used for monochromatic radiation with either a mercury quartz arc, operated at constant current and constant temperature, or an iron arc as a source of radiation. A tungsten filament *F* was mounted inside the tube to provide a source of wave-lengths shorter than those transmitted by quartz.

The iron arc proved to be especially useful for short wave-lengths of monochromatic radiation. Using the mercury arc the photo-electric discharge excited by wave-lengths shorter than 2200A was so small that only under the most favorable circumstances could it be measured with any degree of accuracy. With the iron arc as a source of radiation, measureable deflections of the electrometer were obtained for exciting wave-lengths as short as 1850A. To be sure the radiation that passed the illuminator when the iron arc was the source was not strictly monochromatic. But, the radiation was of sufficient intensity so that the illuminator slits needed to be open not more than 0.5 mm. This gave a narrow range of wave-lengths sufficiently monochromatic for most purposes.

The unsteadiness of the iron arc is its chief disadvantage. The rate at which it radiates energy varies widely in a short time. This disadvantage was overcome by a null method of measurement suggested by Prof. Swann. The incident beam of radiation was interrupted by a small right angled quartz prism and reflected totally on to a comparison disk of platinum. The prism moved to and fro across the beam at right angles to it with a frequency great enough to ensure steady deflection of the electrometer. The beam of incident energy was reflected to the comparison disk as the prism crossed its path. At all other times the energy fell upon the test specimen. The comparison disk was connected to the insulated quadrant of the electrometer. Electrons discharged from the disk tended to neutralize the effect of the electrons fed into the insulated quadrant by the platinum specimen under test. By use of a rotating sector in the path of one of the beams the discharge of electrons from the test specimen was balanced against the discharge from the comparison disk. The area of the sector was adjusted until there was no deflection of the electrometer. The comparison disk received no treatment during the investigation and its photo-electric action remained constant. Since the energies incident upon the test specimen and upon the comparison disk were always of the same wave-length, a comparison of the photo-electric currents produced by them is allowable. The only assumption



involved is that the number of electrons discharged is proportional to the energy which strikes the metal. The angular area in the sector needed to balance the two photo-electric emissions is a measure of the emission from the test specimen in terms of the discharge from the comparison disk. This device was especially useful for determining the form of curves in the short wave-length region. The results obtained with the mercury arc always left doubt as to the shape of the curves in this region.

#### RESULTS OF HEATING FRESH SPECIMENS OF PLATINUM

It is remarked by both Koppius<sup>3</sup> and Tucker<sup>4</sup> that the photo-electric current increases after the platinum has been heated for a time. Suhrmann<sup>6</sup> obtained a very large increase in the photo-electric current per unit incident energy by heating his platinum foil with an electric current. In all three cases the platinum was heated by an electric current through it, the method of heating used by most experimenters, if not by all, who have sought to get rid of gases.

An increase in photo-electric current was observed by the author when a fresh specimen was heated. All the specimens investigated were cleaned by dipping in nitric acid and by heating in a Bunsen flame. After mounting them in the tube none showed a detectable photo-emission when the total radiation from the mercury arc was focused upon them until after being heated by sending an electric current through them. It was not sufficient to heat them in the oven. In some cases the temperature of the baking process was as high as 500°C but in no case did the specimens become photo-active by heating in the oven at this temperature. Heating at a much lower temperature with an electric current through the specimen was sufficient to produce photo-activity. When the comparison disk of platinum, mentioned above, was mounted it gave very feeble emission when the total radiation from the iron arc was focused upon it. The Pyrex tube surrounding it was heated almost to the softening point but this had no effect upon the photo-emission from the disk. Photo-activity was increased by removing the disk from the tube and polishing off its surface with sand paper. It seems to be the experience of all investigators that an untreated specimen of platinum has some sort of layer, probably adsorbed gas, on its surface which hinders the escape of photo-electrons.

The following is a typical case of the behavior of a fresh specimen of platinum when an electric current is sent through it. In this case the tube was not baked but the pressure was reduced to about  $10^{-6}$  mm. There was no emission under the influence of the total radiation from the mercury arc. Currents beginning with 0.1 amp. were sent through the specimen.

The currents were gradually increased with no observable effect until a current of 2 amp. was reached. Then the electrometer began to deflect. The current was kept constant, at 2 amp. and the observations plotted in Fig. 2 were made. (The deflections are in centimeters per 30 seconds observed at the times indicated.) The specimen could not have been heated by this current to a temperature higher than 250°C. This effect was noted many times with several different specimens. It was most pronounced for fresh specimens although it was also observed for specimens after the photo-electric emission had been reduced by prolonged heating. Increase in the photo-electric current is accompanied by a shift of the long wave-length limit toward the red.

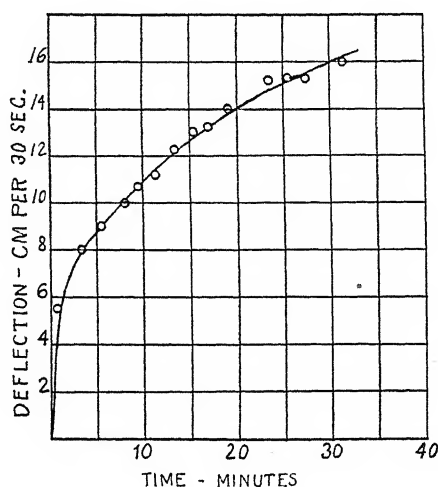


Fig. 2. Recovery of sensitivity to radiation from mercury arc while current of 2 amp. is being sent through a fresh specimen. Pressure  $10^{-6}$  mm.

After the observations plotted in Fig. 2 were made the specimen was allowed to stand over night, the pressure being kept at about  $10^{-6}$  mm. The next morning the rate of deflection was practically the same. When 2 amp. of heating current were sent through the specimen the deflection rose slightly to 15.3 cm. There was no further increase with time. The current was increased to 2.5 amp. and the deflection decreased. Further increase of the heating current decreased the photo-electric current gradually. When the heating current reached 4.5 amp. the deflection was but 4 cm per 30 seconds. The readings were all made with an accelerating potential of 23 volts and with the heating current flowing continuously. When the accelerating potential was reversed the specimen showed a strong discharge of positive ions coming off for heating currents greater than 2 amp. but none for heating currents of 2 amp. or less. This dis-

charge of positive ions was always found present whenever the photoelectric emission was reduced by heating the specimen.

Another specimen was tested for the same effect but in a much better vacuum. This was not a new specimen but it was newly baked to a temperature of  $400^{\circ}\text{C}$ . The pressure was below  $10^{-7}$  mm. Beginning with 0.5 amp. the current was gradually increased to 4 amp. with no observable deflection of the electrometer. The slits of the illuminator were open 1.5 mm. At 4 amp. a slight deflection of the electrometer was observed. Readings were taken for 10 minutes. Then the slits were closed to 0.5 mm and the observations plotted in Fig. 3 were made for 2200, 2300 and 2400 Å. There was an accelerating potential of 14 volts. At the end of the

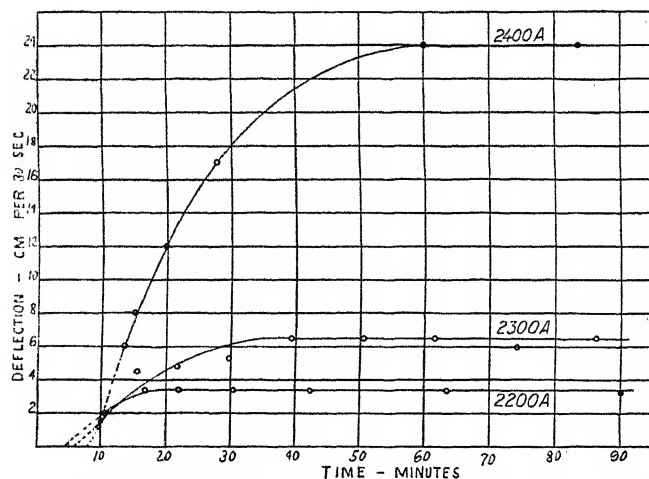


Fig. 3. Recovery of sensitivity to radiation of different wave-lengths while current of 4 amp. is being sent through specimen, previously baked at  $400^{\circ}\text{C}$ .

run the field was reversed but there were no positive ions coming off the specimen. The temperature was estimated to be about  $600^{\circ}\text{C}$  from a previous calibration curve. During the time the observations were in progress the long wave-length limit shifted from a value below that of radiation transmitted by quartz to a value of about 2550 Å.

The current was then increased to 4.5 amp. Immediately the photoelectric current dropped to about 80 percent of the maximum value at 4 amp. The temperature at 4.5 amp. was such that the specimen showed a just detectable faint red glow. When the current was increased to 5 amp. the emission dropped to 20 percent of the maximum value for 4 amp. Reversal of the accelerating field showed a very large emission of positive ions—much too large to be measured on the electrometer.

## THE EFFECT OF PROLONGED HEATING ON THE PHOTO-ELECTRIC EMISSION

One of the most pronounced effects of prolonged heating was that obtained with a specimen treated as follows: The tube was baked at  $280^{\circ}\text{C}$  for two hours. The pumps were kept running during the baking process, the pressure being about  $10^{-6}$  mm. The specimen was then glowed 17 hours at a temperature of  $1300^{\circ}\text{K}$ . When tested for photo-electric emission there was no discharge of electrons even when the total radiation from the mercury arc was focused directly upon the specimen. This condition existed for two months. Often during this time air was admitted in to the tube to atmospheric pressure and pumped out again. Still there was no photo-emission. When the tube was filled with hydrogen and pumped out no effect was produced. Photo-activity was restored by moderate heating with an electric current.

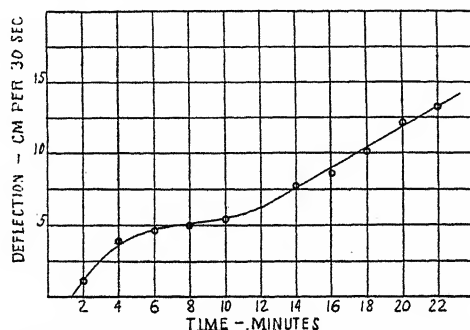


Fig. 4. Typical recovery curve for sensitivity to mercury arc radiation for specimen after prolonged heating at  $1300^{\circ}\text{K}$ . Pressure  $10^{-6}$  mm.

The case just described is the only case in which prolonged heating caused the specimen to be inactive for such a long time. If the heating takes place at lower pressures the photo-emission disappears but returns, for the shorter wave-lengths in a few minutes, for the longer wave-lengths in a few hours at most. The time required for the return depends upon the previous history, the intensity of the heating and the duration of the heating as well as upon the wave-length of the exciting radiation and the pressure of the gas in the tube. A typical recovery curve is shown in Fig. 4. The total radiation was used for excitation. Such a curve may be repeated any number of times simply by heating the specimen for a few minutes to a moderately high temperature.

Fig. 5 shows the recovery of emission for another specimen, monochromatic radiation (2300A) being used for excitation. This specimen had been heated for 15 hours at  $1300^{\circ}\text{K}$ . The pressure during heating

was the lowest obtainable. Before the observations were begun air was admitted to a pressure of  $8 \times 10^{-6}$  mm. The observations were made in order beginning with the smallest heating current. The specimen was heated 5 minutes with 4 amp. of heating current (temperature about  $800^\circ\text{K}$ ). Observations were begun as soon as the heating stopped. Immediately after the observations for the first curve were made the specimen was heated with 5 amp. (temperature about  $1000^\circ\text{K}$ ) for 5 minutes and the observations plotted in the second curve were made. Similarly, the observations for the third curve were made after 7 amp. (temperature about  $1300^\circ\text{K}$ ) had been used to heat the specimen. An iron arc was used as a source of radiation. The illuminator slits were open 0.5 mm. It is seen from these curves that a higher maximum is reached each time the specimen is heated. When 8 amp. were used the recovery curve was broken and irregular and after several hours the total emission had not reached the former maximum for 7 amp.

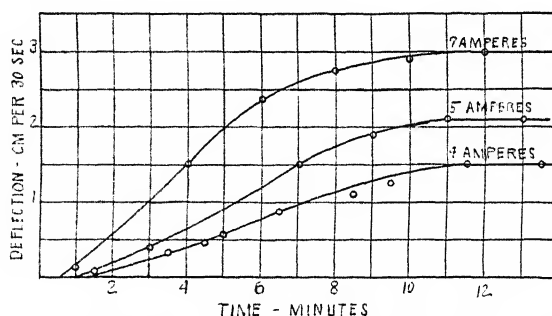


Fig. 5. Recovery of sensitivity to 2300 Å (after heating for 15 hr. at  $1300^\circ\text{K}$ , at lowest pressure) during heating with current of 4, 5 and 7 amp. successively.

The next observations were made to test the recovery of the emission for high vacuum conditions and for different wave-lengths. The specimen last described was used. It was rebaked and allowed to cool and baked again, the pumps running during the baking, until the pressure was too low to be registered on the ionization manometer. The observations plotted in Fig. 6 were made. The process was to heat the specimen with 7 amp. of current (temperature about  $1300^\circ\text{K}$ ) for 5 minutes, then to make the observations immediately. Two exciting wave-lengths were used, 2400 and 2200 Å. An observation was made for one wave-length then the monochromator was changed to the other, and an observation made for it. Thus each pair of curves represents a single recovery of emission but gives the effect with the two exciting wave-lengths. The observations plotted in the three pairs of curves were made in succession, each time the specimen being heated with 7 amp. of current for 5 minutes.

It is noted that the curves do not repeat themselves but that each time the maximum approached is a little less, the order of making the curves being from (1) to (3). This behavior is different from the behavior when the pressure is high. Then the curves can be made to repeat themselves indefinitely. Aside from the fact that there is a difference in pressure it is also to be remembered that in the case where the curves repeated themselves the specimen had been heated several hours by an electric current.

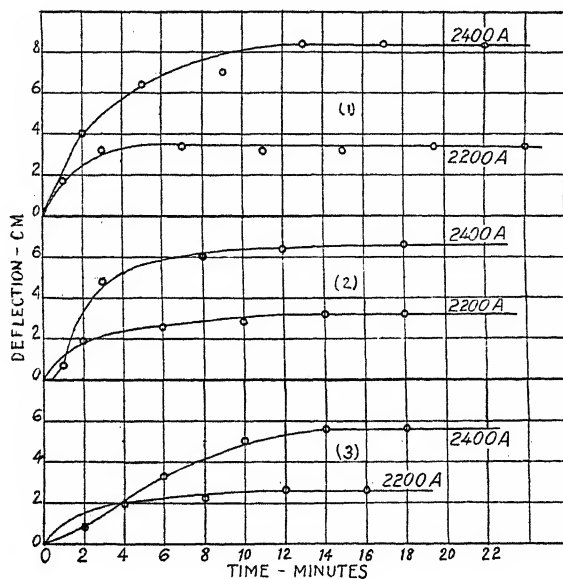


Fig. 6. Recovery of sensitivity to 2200 and 2400 Å, at lowest pressures, after heating to 1300°K for 5 min. The three pairs of curves were made in succession, the specimen being reheated before each pair.

The recovery curves for monochromatic radiation show that the recovery of emission occurs more rapidly for the shorter wave-lengths. This fact is emphasized particularly if the curve for the total radiation, Fig. 4 be examined. The increase in emission is still rapid after 22 minutes. Tucker<sup>4</sup> shows a curve plotted for a period of 2 hours in which the emission has not yet reached a maximum. The later increase in emission is that excited by the longer wave-lengths.

Still another effect of prolonged heating was observed during the latter part of the work after the best technic had been developed for obtaining a vacuum. It was found that a large change in the photo-electric current could be produced with no appreciable change in the long wave-length limit. This change in the photo-electric current was sometimes as much



as a decrease to only one seventh. This decrease in current was brought about by heating the specimen for several seconds at a temperature of about  $1300^{\circ}\text{K}$ . The emission was decreased for all wave-lengths but so far as could be detected there was no shift in the long wave-length limit. This limit was ascertained by setting the monochromator for longer and longer wave-lengths until no deflection could be observed.

The disappearance of the photo-electric emission after prolonged heating is due to the fact that the long wave-length limit has been shifted to a value below that transmitted by quartz. This was proved by mounting a tungsten filament inside the tube. The filament was properly shielded to prevent electrons getting across from it to the test specimen, being completely surrounded by a copper oxide cylinder except for an opening just large enough to allow radiation to pass. As a further precaution a copper plate was placed between the test specimen and the shield surrounding the filament. The efficiency of these devices was shown by the fact that readings taken with a magnetic field perpendicular to the line joining the filament and the test specimen agreed with those taken without the magnetic field. It was found that as the temperature of the filament was increased the radiation from it began to produce photo-emission. This test was tried on the specimen mentioned above which was so long inactive for radiation transmitted by quartz. Although there was no deflection of the electrometer under the influence of the radiation from the mercury arc, when the temperature of the filament was raised the deflection amounted to as much as 300 mm per 30 seconds.

#### THERMIONIC MEASUREMENTS

Thermionic measurements were made on the specimen mentioned in the last paragraph while it was photo-electrically inactive. Before the measurements were begun the tube was newly baked out and the pressure reduced to  $10^{-6}$  mm. The platinum foil was heated for several hours at a temperature higher than any used in the thermionic measurements. The results are plotted in Fig. 7. The value of  $b$ , in the Richardson equation, taken from this graph is  $6.3 \times 10^4$ . This corresponds to a long wave-length limit of 2275A if one assumes that the thermionic and photo-electric work functions are equal. After the thermionic measurements were made the specimen was still photo-electrically inactive under the influence of the total radiation from the mercury arc. However, this fact does not mean, necessarily, that the long wave-length limit of platinum was below 1850A, the shortest wave-length transmitted by quartz, for the intensity of the short wave-length energy may have been too low to give a measurable emission after the platinum had received the treatment



given it. Later investigation, using the iron arc operating on 10 to 12 amp. showed this to be the case.

Thermionic measurements were made on still another specimen. This specimen had been in use several months. It had been baked and glowed repeatedly. Before the thermionic measurements were made it had been standing under atmospheric pressure for several days. The measurements were made at as low temperatures as possible, between 1100 and 1200°K, so as to disturb as little as possible the conditions set up by the previous treatment. Currents were measured with the Dolezalek electrometer, the sensitivity being 1800 mm per volt with a capacity of about 60 cm. Just before the thermionic measurements were begun the tube was well baked and the specimen heated for two hours at a temperature of 1400°K. The pressure was kept below  $10^{-7}$  mm.

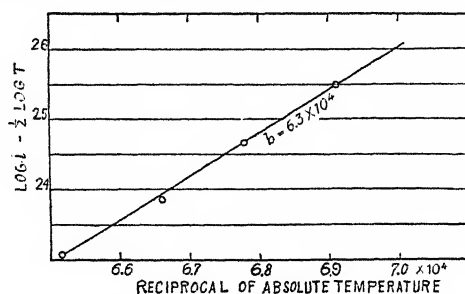


Fig. 7. Plot of thermionic measurements for photo-electrically insensitive specimen, giving value of  $b$  equal to  $6.3 \times 10^4$ .

The value of  $b$  as measured from the line plotted was  $7.1 \times 10^4$ . The specimen stood over night, the pressure remaining below  $10^{-7}$  mm. The next morning it was glowed for one hour at a temperature of 1300°K. The thermionic measurements were repeated for the same range of temperature as the first. The value of  $b$  was  $10.7 \times 10^4$ . In both cases there was no photo-electric discharge of electrons immediately after the thermionic measurements were completed although the iron arc was used as the source of radiation. In the latter case photo-emission for a wave-length of 2200Å was first detectable a few minutes after the heating current had been stopped. There was no emission for longer wave-lengths. The next morning the long wave-length limit had shifted toward the red so that the emission produced a deflection of 300 mm per 30 seconds for the wave-length 2400Å. Other thermionic measurements at these low temperatures gave values of  $b$  abnormally high for specimens that had been heated for long periods.

These high values of  $b$  must have been due to surface conditions which were set up by the treatment given the foil. They were repeated a

sufficient number of times, to ensure that they were not accidental. Each time photo-electric observations showed that there was no photo-electric emission if the foil were tested immediately after the thermionic measurements were completed. This was true even when the total radiation from the iron arc was focused on the foil. This surface condition was decidedly unstable. This is shown by the fact that if one began the measurements of thermionic current at the lowest temperature and proceeded to higher temperatures the points fell accurately on a straight line when  $(\log i - \frac{1}{2} \log T)$  was plotted against  $1/T$ , but if one returned to lower temperatures after measuring the current for higher values the points corresponding to the lower temperatures did not, in general, fall on the same line with the formerly obtained points.

Since the photo-electric long wave-length limit below 2200A could not be measured the equality of the thermionic and photo-electric work functions could not be determined. The thermionic measurements show only that whenever there is a decrease in the long wave-length limit brought about by treatment, there is a corresponding increase in the value of  $b$  of sufficient magnitude in all cases to account for the known decrease in the long wave-length limit if the equality of thermionic and photo-electric functions be assumed.

#### EFFECT OF ELECTRIC FIELDS UPON THE LONG WAVE-LENGTH LIMIT

An attempt was made to measure the velocity of the photo-electrons from a specimen that had been heated for a long period. One specimen which had been heated repeatedly was producing a deflection of 180 mm per 30 seconds with the total radiation from the mercury arc for excitation and with an accelerating potential of 30 volts. The pressure was about  $10^{-6}$  mm. It was found that 0.06 volt was sufficient to stop all photo-electrons from the specimen. The retarding potential was increased to 2 volts. When it was removed and the specimen earthed no electrons came from the specimen when the total radiation from the mercury arc was focused upon it. When the accelerating field was reapplied the emission reappeared immediately to the full previous value. This process was repeated several times. The phenomenon was noted with several specimens. It was more pronounced with rather high pressures, that is with pressures of  $10^{-5}$  mm, than with pressures of  $10^{-7}$  mm, although it was present at the latter pressure. At the lower pressure there was a tendency for the specimen to remain inactive for wave-lengths above, say, 2200A. Applying an accelerating field restored the emission for the longer wave-lengths. The disappearance and restoration of the photo-

activity took place very rapidly. A double throw switch was arranged so that the change could be made from retarding field to accelerating field quite quickly. With retarding potentials as small as 0.01 volt the change could not be made rapidly enough to get a deflection of the electrometer after the retarding field was thrown on. This effect was obtained with several different specimens. It occurred only with specimens that had been heated for long periods of time, 15 to 30 hours. Tests made on unheated and slightly heated specimens did not show this effect.

#### CONCLUSION

The results of this investigation show that the initial heating of a specimen with an electric current shifts the long wave-length limit toward the red and increases the photo-electric current. This is in agreement with the results obtained by observers already quoted. The shift in the long wave-length limit and the increase in the photo-electric current may be accounted for by assuming that initially there is an adsorbed layer of gas on the surface which retards the escape of the photo-electrons. If there is such a layer of gas it may be removed by heating the platinum to a temperature of 250°C with an electric current through it. The gas is not removed by heating to 500°C in an oven. Possibly these facts may be reconciled when it is considered that all parts of the apparatus were cold when the electric current was used for heating. The gas could escape more easily than when all the apparatus was hot. Tests show that the gas discharged is not ionized.

The results of prolonged heating cannot be so readily accounted for. A first glance at the curves of Figs. 4, 5 and 6 would indicate that the Wiedmann-Hallwachs' theory is correct. Closer inspection shows that this is not the case. If the recovery of photo-activity were due to re-absorption of the gas then it should take place much more rapidly for the high pressures of Fig. 5 than for the very low pressures of Fig. 6. This is not the case. Furthermore, if the re-absorption of gas is to account for the recovery of emission the final value of the photo-electric current should depend only upon the amount of the absorbed gas. Fig. 5 shows that the final value increases as the current used to reduce the emission is raised. Fig. 6 shows that the final value is decreased as the process of heating is continued. As mentioned above, after the observations plotted in Fig. 5 were made 8 amp. were used to heat the specimen. The result was a very slow recovery which did not reach the previous maximum value after several hours. It is difficult to see how this could occur if the recovery is due to re-absorption of gas. The curves of Fig. 5 show, rather, that each time the specimen was heated more of the absorbed

and adsorbed gas was liberated. The result was an increase in the photo-electric current.

The decrease of emission to zero during the heating appears to be caused by the formation of a different sort of surface layer. The decomposition of this layer allows the photo-electric current to return, not to its former value but to a higher value which is made possible by the removal of the original gases from the surface. When 8 amp. were used as a heating current the surface layer formed was less temporary and it prevented the return of the photo-electric emission to the previous maximum value. The same sort of process is indicated by the results plotted in Fig. 6. Here as the heating is continued the final value of the photo-electric current gradually decreases. The thermionic investigation confirms these conclusions.

Further proof of the formation of some sort of retarding surface layer is furnished by the effects produced by small electric fields. An electric field could not remove or deposit, instantaneously, a layer of gas, but it could alter the arrangement of an ionic layer on the metal surface so as to make it a retarding influence.

Large decreases or increases of photo-electric current with no change in the long wave-length limit, or with insufficient change to produce the variation in the photo-electric current, may be accounted for by the formation of the retarding layer in patches on the surface of the platinum. Other areas are uncovered and continue to emit with the same or with little changed long wave-length limit. Thus the total photo-electric current is reduced but the long wave-length limit remains constant. This condition occurred in the author's investigations only when the gas pressures were the lowest. This fact would indicate that the retarding layer is formed from the residual gas in the tube. When the pressure is very low there may not be sufficient gas to form a layer which completely covers the surface of the metal.

The author wishes to acknowledge his indebtedness to the staff of Ryerson Laboratory, especially to Prof. W. F. G. Swann. It was under Prof. Swann's direction that this work was completed.

RYERSON LABORATORY,  
UNIVERSITY OF CHICAGO,  
January 1, 1925.

## INVESTIGATION OF PHOTO-ELECTRIC VALVE COATED WITH POTASSIUM

BY V. M. ALBERS

## ABSTRACT

Study of dumb-bell valve coated with potassium.—The tube used by Tykociner and Kunz has been studied more thoroughly. In the case of a transparent deposit on the connecting tube, curves are given showing the current through the tube when illuminated  $I_l$ , and when dark  $I_d$ . The ratio  $I_l/I_d$  reached a minimum at 40 and at 300 volts. The difference reached a maximum for a potential difference of 200 volts. The current increased linearly with light intensity at first and then less rapidly, approaching a saturation value. With an opaque film of potassium, illuminated through a window, the current increased in proportion to the voltage to 1000 volts and also in proportion to the light intensity. Evidently the thicker film gave the more efficient valve. Tests with dispersed light showed that with both transparent and opaque films, the current per unit energy decreased rapidly with increasing wave-length, reaching zero at between 520 and 540  $m\mu$ . In explanation of these effects it is suggested that photo-electric emission from the film reduces the accumulation of electrons on the wall which tends to stop the current through the tube by electrostatic repulsion. However, this does not explain the variation of the effect with wave-length.

THE purpose of this investigation was to make a thorough study of the photo-electric phenomena discovered by Professor Tykociner and Professor Kunz.<sup>1</sup> They discovered that an electron current passing through a tube which had a transparent film of potassium deposited on its walls, would be amplified if the tube was exposed to light. They also found that the effect was selective, the amplification depending on the wave-length as well as on the intensity of the light used to illuminate the tube.

J. M. Hyatt<sup>2</sup> studied the effect using visible films of potassium on the tube through which an electron current from a heated filament was passed. He found that illumination of the tube caused an increase in the current, and also that if the voltage across the tube was maintained at a constant value and the filament current increased, the current through the tube increased to a maximum and then suddenly decreased to a minimum from which it increased very slowly with increase in filament current.

<sup>1</sup> Tykociner and Kunz, Science 59, 320 (April, 1924).

<sup>2</sup> J. M. Hyatt, Phys. Rev. 38, 501 (April, 1924).

## APPARATUS

The tube used by Tykociner and Kunz was employed also in the present investigation. It consisted of two bulbs each about 5 cm in diameter, connected together by means of a tube 2 cm in diameter and 12 cm long (see Fig. 1). There was quite a heavy deposit of potassium on the inside of the bulbs and the connecting tube was treated by first depositing a film of potassium on it and then gently heating it until there was no visible film left.

The source of current through the tube was an oxide coated filament which was heated by means of a 6 volt storage battery  $B$ , and its temperature was kept constant by keeping the current, as read by the ammeter  $A$ , constant to within 0.02 ampere. The potential across the tube was furnished by dry cells for voltages below 100 volts and by a motor-generator set  $G$  for the higher voltages. The current through the tube

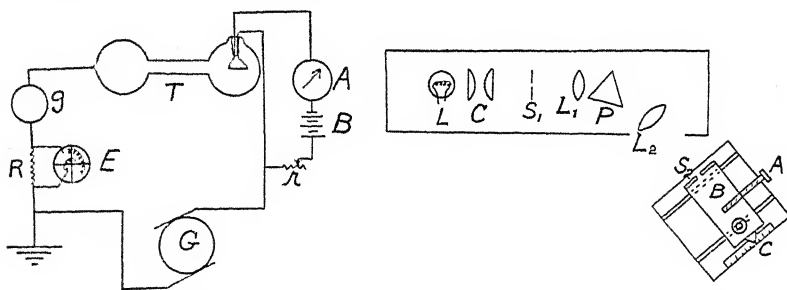


Fig. 1. The valve and the electrical connections. Fig. 2. The optical system.

was measured by means of the galvanometer  $g$  for the larger currents or a quadrant electrometer  $E$  for the smaller currents.

The tube was inclosed in a light tight box which had an adjustable opening, the same length as the connecting tube in the side of the box. The two bulbs were shielded, as far as possible, from the light that was used to illuminate the connecting tube. The source of light  $L$ , Fig. 2, was a 400 watt incandescent lamp which was supplied with a current of 3.7 amperes. A condenser  $C$  was so placed that it brought the light to a focus at a slit  $S_1$  used to cut out all stray light. By means of the lenses  $L_1$  and  $L_2$  and the prism  $P$  the light was dispersed into a spectrum and focused on  $S_2$ . The platform  $B$ , which carried the slit and the tube, could be moved at right angles to the direction of the beam of light passing through  $L_2$ , by means of the screw  $A$ . The position of the slit could be read by means of the scale  $C$ .

A spectrometer was used to measure the wave-length of the light passing through  $S_2$  for several different positions and the calibration curve



was plotted. A thermocouple was then fastened to the slit  $S_2$  and readings of the deflections of the thermocouple galvanometer for corresponding positions of the slit were taken so that the curve showing the relation

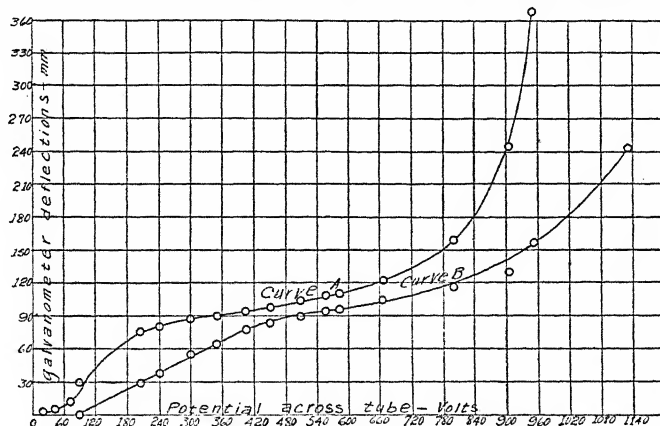


Fig. 3. Current-voltage characteristic curves when the tube is illuminated (Curve A) and when it is dark (Curve B).

between the energy passing through the slit and the wave-length of the light falling on the slit could be plotted.

#### EXPERIMENTAL RESULTS

1. Current-voltage characteristics with a transparent film of potassium on the connecting tube were taken when the tube was dark and when it

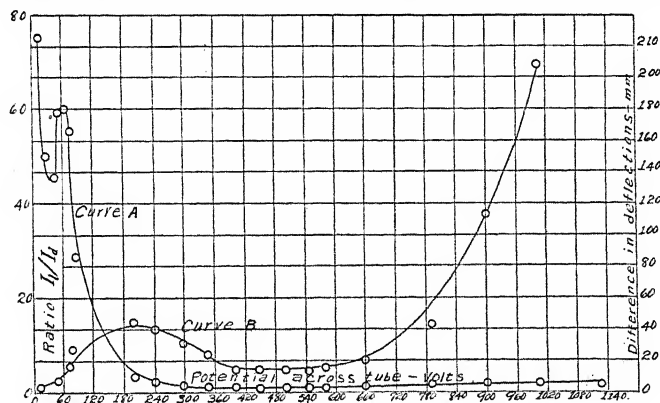


Fig. 4. Curve A shows the relation between  $I_l/I_d$  and the potential. Curve B shows the relation between  $\Delta I$  due to illumination and the potential.

was illuminated (Fig. 3). From these curves the ratios of the current when the tube was illuminated  $I_l$  to the current when the tube was dark  $I_d$  were calculated for each value of the voltage (Fig. 4, curve A).



The value of the ratio was found to decrease very rapidly from zero volts to about 40 volts, then to increase very rapidly with increase in voltage for a short range and then to decrease again to a minimum value from which there was very little change. These curves changed a little in the course of time, probably because the thickness of the film of potassium in the connecting tube was continually changing, but the minimum always appeared at the same voltage. The change in the current due to illumination  $\Delta I$  was also plotted as a function of the voltage (Fig. 4, curve B). When the tube was illuminated without the filament being heated no current could be detected through the tube; this shows that the increase in current when the filament is heated and the tube illuminated is not simply a photo-electric current added to the thermionic current.

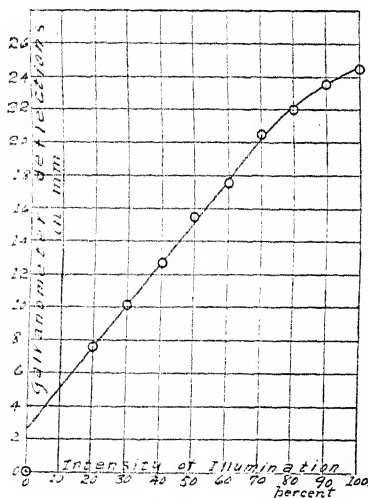


Fig. 5. Relation between the current through the tube and the light intensity.

2. In order to study the effect on the current of variation of the intensity of illumination of the tube, when the voltage was kept constant, a set of rotating sector disks was used. The maximum light intensity (no disk) was about 100 foot-candles. The light intensity was varied in steps of 10 percent each. The curves (Fig. 5) show that the current increases at first linearly with the intensity but at higher intensity bends over toward a saturation value. The results indicate that this saturation value appears for greater light intensity with low voltages than with high voltages.

It was impossible to get accurate enough data to plot curves for voltages above 200 volts because the values of  $\Delta I$  were so small compared

to the value of the current through the tube when it was dark that no appreciable difference in deflection could be obtained even for a change of ten percent in the intensity of illumination.

3. In order to study the amplification produced by different wave-lengths of light, the tube was mounted vertically on the platform *B* (Fig. 2), far enough away from the slit (26.5 cm) so that the light which passed through the slit would illuminate the entire connecting tube.

Measurements of the increase in deflection  $\Delta I$ , as read on the electrometer, were divided by  $E$ , the reading of the thermocouple galvanometer for the same position of the slit, in order to determine the increase in current per unit energy (in arbitrary units). Values of  $\Delta I/E$  were found

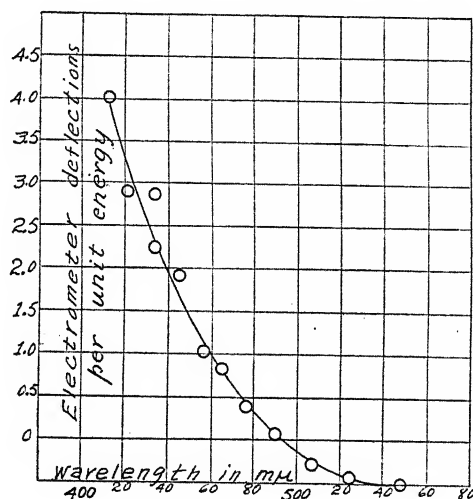


Fig. 6. Relation between the deflections per unit radiant energy and the wave-length of the light used.

for wave-lengths between 416  $m\mu$  and 550  $m\mu$  (see Fig. 6). For wave-lengths shorter than 416  $m\mu$  the amount of energy passing through the slit was too small to give an accurate calibration with the thermo-couple. The curves for different voltages and for different thicknesses of the film of potassium on the connecting tube all have the same general shape as the one shown in Fig. 6. It is interesting to notice that the curves show no maximum value for  $\Delta I/E$ , while an ordinary photo-electric cell has a maximum at about 440  $m\mu$ .

4. The current-voltage characteristics were taken for the same tube having a visible film of potassium on the walls of the connecting tube. This was deposited by heating one of the bulbs, which contained some

potassium. A window was then made in one side of the connecting tube by heating it at one point until the glass became clear at that point.

The same measurements were made with the tube in this condition as were made when the film was invisible except that it was impossible to measure the values of the current through the tube when it was not illuminated because it was of the same order of magnitude as the leaks in the circuit. It was also found that the current-voltage characteristics for the tube, when it was illuminated, were very nearly a straight line; in one case it was found that a straight line fits the points better than any other curve. It is interesting to notice that the tube with a visible film of potassium on its walls is a more perfect valve than the same tube with an invisible film of potassium on its walls. Also with the film of potassium thick enough to be visible no saturation value was found even for voltages as high as 1000 volts, in fact, the curves are almost straight lines.

5. The effect of the light intensity and the wave-length of the light on the current was the same as in the case of the invisible film.

#### DISCUSSION OF RESULTS

In seeking an explanation for these phenomena it is suggested that, when there is a stream of electrons passing through the tube, some of the electrons would strike the sides of the tube and remain there. This would cause the walls of the tube to become charged, which would have the effect of focusing the electrons down to a narrow beam and would also decrease the effective voltage across the tube. When the walls of the tube are illuminated, the potassium, being photo-electric, will emit electrons and thereby lose a part or all of this negative charge, and when this happens the two effects of the charged walls will be reduced or eliminated. The reduction of the effect of the focusing of the beam of electrons will cause the resistance of the tube to decrease which will cause an upward shifting of the current-voltage characteristic curve. The reduction of the charge on the walls of the tube will cause the repulsion of electrons back toward the filament to be decreased and this will have the same effect as an increase in voltage across the tube so it will cause a shift of the current-voltage characteristic curve toward the left. We might also try to explain these phenomena by the difference in the reflection of the electrons from the walls of the tube when they are charged and when they are uncharged.

Two interesting facts are not yet understood: (1) The distinct minimum found in the curves showing  $I_i/I_a$  plotted as a function of the voltage; and (2) the absence of a maximum at about 440 m $\mu$  in the curve

showing the relation between the wave-length of the light and the current through the tube.

ACKNOWLEDGMENTS

In conclusion, I wish to express my thanks to Professor J. Kunz, who made this work possible with his valuable help and suggestions, and to Professor A. P. Carman for the laboratory facilities which were so kindly placed at my disposal.

DEPARTMENT OF PHYSICS,  
UNIVERSITY OF ILLINOIS,  
June 10, 1925.

## A MATHEMATICAL TREATMENT OF THE ELECTRIC CONDUCTIVITY AND CAPACITY OF DISPERSE SYSTEMS

### II. THE CAPACITY OF A SUSPENSION OF CONDUCTING SPHEROIDS SURROUNDED BY A NON-CONDUCTING MEMBRANE FOR A CURRENT OF LOW FREQUENCY<sup>1</sup>

BY HUGO FRICKE

#### ABSTRACT

*Mathematical theory.*—The following formula for the specific capacity  $C$  of the suspension, i.e., the parallel capacity of a one centimeter cube of the suspension, is derived in terms of the capacity  $C_0$  of one cm<sup>2</sup> of the membrane surrounding the spheroids, the major axis  $2q$  of a spheroid, the specific resistances  $r$  and  $r_1$  of suspension and suspending phase, and a constant  $\alpha$  which depends only on the axis ratio  $a/b$  of the spheroid:  $C = C_0 \alpha q (1 - r_1/r)$ . The values of  $\alpha$  are given in a table. One application of the formula is the determination of the thickness of interphasial membranes (biological, adsorptive, chemical). The formula can also be used for a suspension of polarizable homogeneous spheroids when the polarization resistance is small compared to the impedance of the polarization capacity.

#### INTRODUCTION

IN the following discussion the specific electric capacity of a disperse system is defined as that capacity which when combined in parallel with a certain resistance electrically balances one centimeter cube of the system. The present discussion applies to the case in which the capacity is due to phenomena at the interphases of the system, especially as in biological tissues, the capacity of which, as is well known, is usually very high. The capacity may be due to either or in part to each of two different causes: (1) a polarization at the interphases, and (2) the presence in the interphases of thin poorly conducting membranes which act as static condensers. The calculation presented here applies to the first case only if the polarization resistance is small compared to the impedance of the polarization capacity. The general case, when they are of the same order of magnitude, will be considered in Part III of this series of papers.

In this presentation we shall derive a formula by which we can determine from the capacity and resistance of a suspension of spheroids and their geometrical form the capacity per unit of surface of the suspended particles. One interesting application of the formula is the calculation of the thickness of the membrane when the capacity is due entirely to the

<sup>1</sup> For Part I, see Hugo Fricke, *Phys. Rev.* **24**, 575-587 (1924).

static capacity of membranes on the surface of the suspended particles. As will be shown in the following paper, this condition is probably realized for the case of blood, and, accordingly, we derive the value of about  $3 \times (10)^{-7}$  cm as the thickness of the membrane, which surrounds the red corpuscle, using a probable value for the dielectric constant of the membrane. This method will probably be useful also for the case of many non-biological suspensions, such as graphite suspensions, which contain well conducting particles surrounded by poorly conducting films, produced by chemical or adsorptive processes.

The fact that capacity of the type here considered is mainly dependent on the state of the interphases, makes it probable that this may be an important characteristic of the colloid properties of the system; especially may we expect this to be true for the case of biological systems. As a matter of fact, investigations which have been carried out in this laboratory have confirmed this belief. It may, for instance, be mentioned that it is found that the capacity of a tumor bears a rather constant relation to its malignancy, this relation appearing so constant that it seems probable that the measurement of the capacity may provide a very practical method for diagnosing the malignancy of a tumor.<sup>2</sup>

#### MATHEMATICAL THEORY

We shall first consider the case of a suspension of particles of any form (volume concentration being  $\rho$ , and number of particles per cc being  $n$ ), each particle in which is surrounded by a non-conducting membrane of uniform thickness  $t$ , and uniform dielectric constant  $K$ . The capacity of this membrane per square centimeter is  $C_0 = K/4\pi t \cdot (10^{-5}/9)\mu\text{f}$ . The resistance of the interior of a particle for the frequencies to be considered is supposed to be small compared with the impedance represented by the static capacity of the surface membrane. We shall call the specific conductivity of the suspending medium  $k_1$  and of the suspension  $k$ . If furthermore,  $\overline{F}^2$  is the average value of the square of the electric force in the suspending medium, we have

$$(1 - \rho)k_1\overline{F}^2 = k V^2. \quad (18)$$

This equation expresses the fact that the heat developed in the suspension by the electric current is equal to the heat developed in a homogeneous conductor with the conductivity  $k$  for the same driving potential  $V$ . We shall now assume, following thereby in principle the method employed in Part I,<sup>1</sup> that the average value of electrostatic energy which is present at the surface of each suspended particle is obtained by placing the particle in a homogeneous field of force equal to  $\sqrt{\overline{F}^2}$ . Evidently this

<sup>2</sup> Hugo Fricke and Sterne Morse, The Electric Capacity of Tumors (in press).



electrostatic energy is proportional to  $C_0$  and to  $\bar{F}^2$ , say equal to  $NC_0\bar{F}^2$ ; consequently we have, if  $C$  is the capacity of the suspension in microfarads,

$$\frac{1}{2}CV^2 = n N C_0 \bar{F}^2. \quad (19)$$

By Eqs. (18) and (19)

$$C = 2N C_0 \left( \frac{k}{k_1} \right) \left( \frac{n}{1-\rho} \right) \quad (20)$$

Here  $N$  is dependent only on the constants which define the single suspended particle geometrically.

We shall now proceed to calculate  $N$  for the case of a suspension of spheroids. The electric forces in the suspending liquid are obtained by means of the equations given in Part I using  $k_2 = 0$ . Since the potential inside the corpuscle is constant, the resistance of the inside of the corpuscle having been assumed low as compared with the impedance of the membrane,  $V_{\text{int}}$  of Eq. (6) Part I, represents the potential difference between the two sides of the membrane. The average total static energy at the surface of a spheroid, arbitrarily placed in a homogeneous field of strength unity is consequently

$$N C_0 = \int_{\pi}^0 \frac{\cos^2 \varphi d(2\pi \cos \varphi)}{4\pi} \cdot \frac{1}{2} C_0 \sum (a \neq a, b, b) \int \frac{4x^2 dS}{(2 - ab^2 L_a)^2}$$

$\varphi$  being the angle between the direction of the field and one of the axes of the spheroid. Hence

$$N C_0 = \frac{2}{3} C_0 \left[ \frac{C_a}{4M^2} + \frac{2C_b}{(2-M)^2} \right] \frac{4}{3} \pi ab^2 \cdot a \quad (a < b)$$

$$\begin{aligned} C_a &= \int (\text{over surface of spheroid } x \neq a) \left( \frac{x^2 dS}{\frac{4}{3} \pi a^2 b^2} \right) \\ &= \frac{3}{4} \left[ 1 + \frac{1}{2} \left( \frac{a}{b} \right)^2 \frac{1}{e^2} - \frac{1}{2} \left( \frac{a}{b} \right)^4 \frac{1}{e^3} \log \frac{b}{a} (1+e) \right] \quad (\text{when } a < b) \\ &= \frac{3}{4} \left[ 1 - \frac{1}{2e^2} + \frac{1}{2} \frac{a}{b} \frac{1}{e^3} \arcsin e \right] \quad (\text{when } a > b) \end{aligned}$$

$$\begin{aligned} C_b &= \int (\text{over surface of spheroid } x \neq b) \left( \frac{x^2 dS}{\frac{4}{3} \pi a^2 b^2} \right) \\ &= \frac{3}{4} \left( \frac{b}{a} \right)^2 \left[ 1 + \frac{a}{b} \frac{1}{e} \log \frac{b}{a} (1+e) \right] - \frac{3}{8} \left( \frac{b}{a} \right)^2 \times \\ &\quad \left[ 1 + \frac{1}{2} \left( \frac{a}{b} \right)^2 \frac{1}{e^2} - \frac{1}{2} \left( \frac{a}{b} \right)^4 \log \frac{b}{a} (1+e) \right] \quad (\text{when } a < b) \end{aligned}$$



$$= \frac{3}{4} \left( \frac{b}{a} \right)^2 \left[ 1 + \frac{a}{b} \frac{1}{e} \arcsin e \right] - \frac{3}{8} \left( \frac{b}{a} \right)^2 \left[ 1 \frac{1}{2e^2} + \frac{1}{2} \frac{a}{b} \frac{1}{e^3} \arcsin e \right] \quad (\text{when } a > b)$$

In these equations

$$e = \sqrt{1 - a^2/b^2} \quad (a < b); \quad e = \sqrt{1 - b^2/a^2} \quad (a > b).$$

Consequently ( $\frac{4}{3}\pi ab^2n$  being equal to  $\rho$ ),

$$C = \frac{4}{3} C_0 \frac{k}{k_1} \cdot \frac{\rho}{1-\rho} a \left[ \frac{C_a}{4M^2} + \frac{2C_b}{(2-M)^2} \right]$$

(For the value of  $M$  see Part I, p. 581.)

By Eq. (13) ( $k_2=0$ ):  $(\rho)/(1-\rho) = (k-k_1)/\beta k$ . Introducing furthermore

$$\alpha = -\frac{4}{3}\beta \left[ \frac{C_a}{4M^2} + \frac{2C_b}{(2-M)^2} \right] \left( \frac{a}{b} \right) \quad \text{when } a < b.$$

$$\text{and } \alpha = -\frac{4}{3}\beta \left[ \frac{C_a}{4M^2} + \frac{2C_b}{(2-M)^2} \right] \quad \text{when } a > b,$$

and substituting resistances ( $r, r_1$ ) for conductivities ( $k, k_1$ ) we obtain

$$C = a (1 - r_1/r) q C_0 = C_{100} (1 - r_1/r) \quad (21)$$

$C_{100}$  being the (imaginary) capacity of the 100 percent concentrated suspension, or

$$C_0 = \frac{C}{aq(1-r_1/r)} \quad (22)$$

in which  $2q$  represents the major axis of the spheroid. The values of  $a$

TABLE I  
Values of  $a$  as a function of  $b/a$  and of  $a/b$ .

$b/a:$	1	2	3	4	$\infty$
$a:$	1.50	1.30	1.27	1.28	1.65
$a/b:$	1	2	3	4	$\infty$
$a:$	1.50	1.03	0.94	0.94	(.118 $\times a/b$ )

are given for different values of  $b/a$  in Table I. An experimental verification of the formula will be presented in the following paper.

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CLEVELAND CLINIC FOUNDATION,  
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## THE ELECTRIC CAPACITY OF SUSPENSIONS OF RED CORPUSCLES OF A DOG

HUGO FRICKE

## ABSTRACT

Measurements were made with a bridge, using a substitution method whereby the suspension is indirectly compared with a diluted serum which has the same specific resistance as the suspension. The bridge may be used with frequencies ranging from 800 to 4,500,000 cycles and its sensitivity is such that a capacity in parallel to 100 ohms can be measured with an accuracy of a few  $\mu\text{mf}$  at the lowest frequency. Measurements with a frequency of 87,000 cycles per sec. were made of suspensions of red corpuscles of a dog with volume concentrations between 10 and 88 percent, confirming the formula  $C(\rho) = C_{100}(1 - r_1/r)$  previously derived.<sup>1</sup> By these measurements and the previous formula  $C_0 = C_{100}/ag$  the capacity per  $\text{cm}^2$  of surface of a red corpuscle is calculated to be .81 $\mu\text{f}$ . This capacity is independent of frequencies between 3600 and 4,500,000 cycles and is also independent of the suspending liquid. It is probably the static capacity of the membrane which surrounds the corpuscle. According to this assumption and using 3 for the dielectric constant, the thickness of the membrane is  $3.3 \times 10^{-7}$  cm (monomolecular).

THE following experiments illustrate the application of the theory which was presented in the preceding paper<sup>1</sup> and confirm it.

The capacity, which for a one centimeter cube of normal blood is of the order of a few hundred micromicrofarads in parallel with a resistance of a few hundred ohms, was measured with a specially designed bridge over a range of frequencies from 800 to 4,500,000 cycles. The sensitivity of the bridge is such that such a capacity can be measured with an accuracy of a few  $\mu\text{mf}$  at the lowest frequency. Two arms of the bridge contain a Kohlrausch slidewire which is always used near its middle point; the third arm contains a decade resistance box  $R_1$  (General Radio Company) with a decade condenser in parallel, and the fourth arm the electrolytic cell with a variable condenser  $C_r$  (General Radio standard condenser) in parallel. By means of a switch the electrolytic cell can be replaced by a decade resistance box  $R_r$  similar to  $R_1$ . The coils in the resistance boxes are wound by the Ayrton-Perry method and their effective inductances are rather low.

The current to the bridge is delivered by an audion oscillator and the heterodyne method of detection is employed, using three stage amplification. The bridge is connected to generating and heterodyne oscillation

<sup>1</sup> H. Fricke, preceding paper in this issue.

and to the detector tube by very loose inductive couplings. The electrolytic cell has the form of an hour-glass with large platinized platinum electrodes sealed into the glass at the ends; it is designed to have the lowest possible amount of polarization at the electrodes. The electrode area is between 10 and 20 cm<sup>2</sup>; the distance between the electrodes between 5 and 10 cm. The cell constant is about 1. Effective stirring, which is essential, is accomplished by gently blowing through two glass tubes which are sealed to the top of the cell.

The abstract of the protocol, given in Table I, will explain the experimental procedure. The cell filled with the suspension is compared with the resistance box  $R_r$ ; the difference between the settings of the condenser

TABLE I

*Partial abstract of prot col for blood (11.1%)*

	Units	Exp. IV <sub>1</sub>		Exp. IV <sub>2</sub>		Diluted serum	
$R_1'$ (cell in)	ohms	93.3		93.2		93.1	
$C_r'$	arb.	6.47		6.61		8.08	
Setting of slide wire		+1		+7		-1	
$R_r''$ ( $R_r$ instead of cell)	ohms	93.9	93.8	93.7	93.6	93.7	93.8
$C_r''$	arb.	10.05	10.43	10.26	10.68	10.72	10.40
Setting of slide wire		-14.5	+7	+2.5	+24.5	0	-17.5
Temperature		23.30°	.....	23.20°	.....	22.40°	.....
$C_r'' - C_r'$	$\mu\mu\text{f}$	217	240	222	247	160	141
Total inductance $L$	$10^{-10}\text{h}$	11790	11650	11480	11300	11480	11650
Equivalent capacity ( $L/R_r''^2$ ). $10^2$	$\mu\mu\text{f}$	134	132	130	129	130	132
Capacity corrected for inductance	"	83	108	92	118	30	9
Corrected for difference in slide-wire setting	"		101		97		29
Corrected for static capacity of electrolytic cell	"		95		91		21
Capacity for cell filled with serum	"		21		21		
Capacity of blood	"		74		70		

$C_r$ , ( $C_r'' - C_r'$ ), gives an uncorrected value for the capacity of the suspension. This value is first corrected for the inductance of the coils used in the resistance box  $R_r$  and for the difference between the inductances of the leads which connect the cell and  $R_r$  respectively to the bridge; this correction for our case is  $(L/R_r^2)$  farad, when this total inductance  $L$  is in henries. A small correction is thereafter introduced for the static capacity of the electrolytic cell, which, when filled with a homogeneous liquid of dielectric constant  $K$ , is  $K/4\pi c'$  cm in which  $c'$  is the cell constant equal to the ratio of resistance to specific resistance. For the case of a suspension with a non-conducting disperse phase, like blood,  $K$  is the dielectric constant of the suspending liquid (for blood therefore about 81) and  $c'$  is the constant of the electrolytic cell  $c$  times  $r/r_1$ ,  $r$

and  $r_1$  being the specific resistances of the suspension and the intracellular liquid. Consequently, the static capacity is  $81/(4 \pi c r/r_1) \times (10/9) \mu\text{mf} = 7.2/(cr/r_1) \mu\text{mf}$ .

The value for the capacity thus obtained is still faulty, due to the difference in static coupling between the electrolytic cell and the other parts of the bridge on one side and on the other side between the resistance box  $R_r$  and the other parts of the bridge. The corresponding correction is obtained by making once for all a series of measurements with the cell filled with various dilutions of serum covering the total range of resistances used; the measured capacities are corrected as above and the values which vary very slowly with the resistance, are plotted against the resistance. From this curve a "zero value" for the capacity of the cell is found at the resistance observed in the case of blood which comprises the said difference in static coupling. This "zero value" is subtracted from the value for the capacity as obtained above.

The procedure described above would not have given a correct elimination of a polarization at the electrodes of the electrolytic cell if such an effect had been present to any appreciable amount within the experimental range of frequencies. The frequency at which the polarization becomes appreciable is easily determined by measuring the serum at decreasing frequencies; the setting of the standard condenser remains practically constant until the critical frequency is reached, when an abrupt change takes place.

A confirmation of the accuracy of this method was obtained by making measurements on cream, in which case the resulting capacity is zero. The fact that the value of the capacity of a corpuscle suspension is found to be independent of the form of the electrolytic cell and of the frequency serves as a further confirmation. (The capacity is found to be independent of the frequency between 3600 and 87,000 cycles per sec.; for higher frequencies the capacity decreases due to the fact that the impedance of the static capacity of the corpuscle membrane becomes comparable with the resistance of the corpuscle interior.)<sup>2</sup>

Tables II and III present the results of two series of measurements, typical of several, on the blood of a dog. They include corpuscle concentrations between 10 and 84 percent. The stated volume concentrations were derived from the resistances by an earlier formula<sup>3</sup> ( $a/b = 1/4$ ). The capacity ( $C_{100}$ ) for 100 percent volume concentration is calculated by formula (21) of the preceding paper.<sup>1</sup> The values are constant for

<sup>2</sup> H. Fricke and S. Morse, The electric resistance and capacity of blood for frequencies between 800 and 4,500,000 cycles, *Jour. Gen. Physiol.* (1925).

TABLE II

*Capacity of suspensions of red corpuscles of a dog in own serum.*

Defibrinated blood of dog No. 1 was concentrated by centrifugation, and the concentrated suspension was diluted with serum. Resistance  $r_1$  of serum: 84.25 ohms; temperature: 18.95°C; constant of electrolytic cell:  $c = .98$ .

Frequency: 87000 cycles per sec.

Date: March 22, 1925.

Experiment	Volume concentration	Resistance $r$	Capacity $C$	$C_{100}$ (calc.)	
	(percent)	(ohms)	( $\mu\text{mf}$ )	( $\mu\text{mf}$ )	
I	83.9	931.0	374	411	Concentrated by centrifugation from original blood.
II	21.0	126.9	129	385	From 83.9 percent suspension by dilution.
III	72.0	498.	343	411	From 83.9 percent and 21 percent suspensions.
IV	47.5	230.2	237	374	From 72.0 percent suspension by dilution.
V	60.2	329.	286	385	From 83.9 percent and 47.5 percent suspensions.

TABLE III

*Capacity of suspensions of red corpuscles of a dog in own serum.*

Defibrinated blood of dog No. 1 was diluted with own serum. Resistance  $r$  of serum: 75.8 ohms; temperature: 23.10°C; constant of electrolytic cell: .98.

Frequency: 87000 cycles per sec.

Date: March 23, 1925.

Experiment	Volume concentration	Resistance ( $r$ )	Capacity ( $C$ )	$C_{100}$ (calc.)	
	(percent)	(ohms)	( $\mu\text{mf}$ )	( $\mu\text{mf}$ )	
I	43.9	188.7	232	388	Original blood
II	30.8	140.1	172	374	From original blood by dilution.
III	20.6	113.7	126	378	From 30.8 percent suspension by dilution.
IV	11.1	94.0	72	371	From 20.6 percent suspension by dilution.
V	10.6	93.4	74	391	From original blood by dilution.
VI	42.8	185.3	221	374	Original blood.
Average: $380_{\mu\text{mf}} \pm 2$ percent					

concentrations up to about 60 percent; for still higher concentrations, which approach the stage of total packing for which the theoretical foundation for the formula may be doubtful, there may be a slight tendency to an increase. Using the lower concentrations alone, we obtain  $380\mu\text{f}$  as the average value of  $C_{100}$ . Since the constant of the electrolytic cell is .98 (=resistance/spec. resistance), the specific value of  $C_{100}$  (corresponding to a one centimeter cube) is  $380 \times .98 = 372\mu\text{f}$ .

Using  $a/b = 1/4$  as in our earlier paper<sup>3</sup> and taking  $7.2(10)^{-4}$  cm for the diameter  $2q$  of the corpuscle, by formula (22) we obtain for the capacity per  $\text{cm}^2$  of the membrane

$$C_0 = C_{100}/aq = 372 \times 10^{-6} / (1.28 \times 3.6 \times 10^{-4}) = 0.81\mu\text{f}.$$

It has been shown elsewhere<sup>2</sup> that the capacity of blood is independent of the frequency between 3600 and 87,000 cycles per sec. For higher frequencies the capacity decreases; this decrease, however, for the experimental range of frequencies (up to 4,500,000 cycles), is satisfactorily explained as due to the impedance of the inter- and intra-cellular liquids, with which the capacity of the corpuscle membrane is in series,  $C_0$  itself being independent of the frequency over the above range. We find also that the capacity is not changed when the corpuscles from defibrinated blood are suspended in Ringer's solution or in an isotonic solution of dextrose.

On the ground of our present, although rather incomplete, knowledge of polarization, such a constancy of the capacity would seem hardly possible if it were due to a polarization at the surface of the red corpuscle. Furthermore,<sup>4</sup> there is much evidence that the resistance of the membrane which surrounds the corpuscle is high as compared with the impedance of the capacity  $C_0$  over our whole experimental range of frequencies; therefore, even with a constant polarization capacity at the surface of the corpuscle, the observed capacity should have decreased as the frequency increased. (The resistance of the membrane may, for instance, be estimated from known data for the diffusion of electrolytes from the serum into the corpuscle.) At present, therefore, it seems probable that the observed capacity is due to the static capacity of the corpuscle membrane. The order of magnitude of the thickness of this membrane, which may be derived on this assumption, is suggestive. By using a value of 3 as the dielectric constant of the membrane (a value which of course is

<sup>3</sup> H. Fricke, *Jour. Gen. Physiol.* 6, 741-746 (1924); *Phys. Rev.* 24, 575-587 (1924), Eq. (13).

<sup>4</sup> H. Fricke, The electric capacity of suspensions with special reference to blood, *Jour. Gen. Physiol.* (1925).



rather uncertain, the more so, since the membrane appears to be monomolecular), we obtain a thickness of  $3.3 \times 10^{-7}$  cm. This value corresponds to a chain of from 20 to 30 carbon atoms. Thus, we evidently arrive at the conclusion that the membrane of the corpuscle is monomolecular.<sup>4</sup>

DEPARTMENT OF BIOPHYSICS,  
CLEVELAND CLINIC FOUNDATION,  
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# INFLUENCE OF A BRANCH LINE UPON ACOUSTIC TRANSMISSION OF A CONDUIT

By G. W. STEWART

## ABSTRACT

*General theory of transmission.*—The ratio of the energy of the incident acoustic energy transmitted with the branch present to that with the branch absent is found to be

$$[(Z_1^2 + Z_1 \rho a / 2S + Z_2^2) + (\rho a Z_2 / 2S)^2] \times [(Z_1 + \rho a / 2S)^2 + Z_2^2]^{-2},$$

where the point impedance of the branch is  $Z_1 + iZ_2$ ,  $\rho$  is the density of the fluid,  $a$  the velocity of sound and  $S$  the area of the conduit. *Application to the Helmholtz resonator and the cylindrical resonator.* The transmission ratios found are respectively,

$$\{1 + [4S^2(k/c - 1/kv)^2]^{-1}\}^{-1} \text{ and } \{1 + (4S^2)^{-1}[k/c - (\sigma \tan kl)^{-1}]^{-2}\}^{-1}$$

where  $k$  is  $2\pi/\text{wave-length}$ ,  $c$  is conductivity of the orifice, and  $V$  and  $\sigma$  are respectively the volume and area of the branch. The theory can be applied to ascertain the transmission, when the acoustic impedance of the side branch is known or it may be used to measure the acoustic impedance of the side branch.

*Theory.* This is a general treatment of the influence of the impedance in a branch line upon the transmission of acoustic energy through a conduit. Assume that the transmission occurs through a conduit of constant areas  $S$ , having one side branch and that the incident plane wave, or rather the source, is undisturbed by the action of the side branch.

The symbols used are defined as follows:  $k$  is  $2\pi/(\text{wave-length})$ ;  $a$ , the velocity of sound;  $t$ , the time elapsed;  $\rho$ , the density of the fluid;  $P = P_0 e^{ik a t}$ , the excess pressure of the incident wave;  $P' = P_0' e^{ik a t}$ , the actual excess pressure at the opening into the side branch;  $X = X_0 e^{ik a t}$ , the volume current (rate of volume displacement) flowing into the side branch;  $Z$ , the point impedance of the side branch, equal to  $P'/\dot{X}$ . The values  $P_0$ ,  $P_0'$ ,  $X_0$  and  $Z$  are, in general, complex.

The pressure at the junction,  $P'$ , is caused by two waves, one from the source and the other from the side branch. The pressure caused by the former in the conduit is  $P$ . The pressure caused by the side branch wave can be determined very readily. Assume that the incident wave in the conduit passes from left to right. The outward volume displacement  $-X$  of the wave from the branch, will, on account of symmetry be divided equally between the conduits right and left. The magnitude of the volume displacement is  $X/2$  and the particle displacement is  $-X/2S$  on the right and  $X/2S$  on the left. The particle velocities are

correspondingly  $-\dot{X}/2S$  and  $\dot{X}/2S$ . If the diameter of the conduit is assumed small in comparison with the wave-length, the wave produced in the conduit may be considered as plane; then the pressure produced in the conduit at the right by  $X$  is  $-\rho a \dot{X}/2S$ . The resulting pressure therefore is

$$P' = P - \rho a \dot{X}/2S. \quad (1)$$

Hence, 
$$P'/P = 1 - \rho a \dot{X}/2PS. \quad (2)$$

Since  $P'/Z = \dot{X}$ , then from (1)  $\dot{X}/P = 1/(Z + \rho a/2S)$ , and (2) becomes

$$P'/P = 1 - \rho a / [(Z + \rho a/2S)2S]. \quad (3)$$

Let  $Z = Z_1 + iZ_2$  where  $Z_1$  and  $Z_2$  are real. Then

$$P'/P = 1 - (\rho a/2S)[(Z_1 + \rho a/2S) + iZ_2]^{-1} \quad (4)$$

and

$$(P'/P)^2 = [(Z_1^2 + Z_1 \rho a/2S + Z_2^2)^2 + (\rho a Z_2/2S)^2] [(Z_1 + \rho a/2S)^2 + Z_2^2]^{-2}. \quad (5)$$

This equation, giving the value of the ratio of transmitted to incident energy in the conduit, is general and is independent of the nature of the branch. In the case of a branch in which  $Z_1 = 0$ , the transmission is, from Eq. (5)

$$(P'/P)^2 = [1 + (\rho a/2S)^2(1/Z_2^2)]^{-1}. \quad (6)$$

*Helmholtz resonator.* In the case of a Helmholtz resonator as a branch, the point impedance  $Z$  is  $(Mi\omega - i/\omega C)$ , wherein  $M$  is the inertance of the opening and  $C$  is the capacitance of the chamber or  $\rho a^2/V$ ,  $V$  being its volume.<sup>1</sup>

As shown previously,<sup>1</sup> the inertance of a channel is its mass divided by the square of its area. If inertance is expressed as  $\rho/c$  then  $c$  is the "conductivity." From this definition, for the channel of length  $L$  and radius  $R$ ,  $c = \pi R^2/L$ . But "end" corrections must be made to  $L$  because the inertance is not included in the length  $L$ . Theoretically this correction is proportional to  $R$  if the channel can be regarded as in an infinite plane wall. Hence the well-known form,  $c = \pi R^2/(L + aR)$ . With this definition of  $c$ , the point impedance is  $i(\rho\omega/c - \rho a^2/V)$ . Hence,  $Z_1 = 0$  and  $Z_2$  is the value in the parenthesis. Substituting in Eq. (6), the fraction transmitted is therefore

$$T = \{1 + [4S^2(k/c - 1/kV)^2]^{-1}\}^{-1}. \quad (7)$$

*A closed tube.* If  $a$  is the velocity of sound,  $X$  the volume displacement of a tube with axis in the  $x$ -direction and with constant cross-section, then the following equations hold for a simple harmonic vibration,  $e^{ikx}$ ,

$$\partial^2 p / \partial x^2 = -k^2 p; \quad \partial^2 \dot{X} / \partial x^2 = -k^2 \dot{X}$$

<sup>1</sup> For a more detailed discussion see Stewart, Phys. Rev. 20, 535 (1922), Eqs. (16) and (22).

The solutions of these equations with the additional relationship

$$\rho \partial^2 \xi / \partial t^2 = -\partial p / \partial x,$$

wherein  $\xi$  is the displacement, gives the following expression

$$\dot{X} = (i\sigma/\rho a) (A_1 \cos kx - A_2 \sin kx) e^{ikat}$$

wherein  $\sigma$  is the area of the tube and  $A_1$  and  $A_2$  are pressure amplitudes. If now the tube is closed at  $x=l$ ,  $\dot{X}$  is there zero and the following relationship can finally be obtained,

$$p/\dot{X} = Z = -ipa/(\sigma \tan kl).$$

Thus, for a closed tube attached as a branch,  $Z_1 = 0$  and  $Z_2 = -\rho a/\sigma \tan kl$ .

But no consideration has been given to the conductivity of the opening into the branch, or  $c$ , which introduces inertance as in the orifice of the Helmholtz resonator and should be added to  $Z_2$ . We then have  $Z_2 = \rho\omega/c - \rho a/(\sigma \tan kl)$  and Eq. (6), or the part of the energy transmitted therefore becomes

$$T = \{1 + (4S^2)^{-1} [k/c - (\sigma \tan kl)^{-1}]^{-2}\}^{-1} \quad (8)$$

Here  $c = \pi R^2/(L + aR/2)$ , the factor  $1/2$  being introduced because there is for the end of the cylinder only one-half the correction needed in the case of the orifice.

*Comparison with experiment.* Eqs. (7) and (8) for the transmission have been tested experimentally and found to agree satisfactorily with theory. The results will be presented in a separate paper. Experimental and theoretical results will also be given for open tubes, orifices and other branches.

*Applications.* The theory can be used (1) for the computation of the transmission of a conduit when the acoustic impedance of the side branch is known and (2) in the experimental determination of the acoustic impedance of a side branch. The first use is simple; the second is more complicated in practice and will be the subject of a further communication.

PHYSICAL LABORATORY,  
UNIVERSITY OF IOWA,  
July 30, 1925.

## THE PHYSICAL REVIEW

### A PRECISION MEASUREMENT OF THE CHANGE OF WAVE-LENGTH OF SCATTERED X-RAYS

BY H. M. SHARP

#### ABSTRACT

According to the quantum theory, the change of wave-length due to scattering is  $\delta\lambda = (h/mc) (1 - \cos \phi)$  where  $h$  is the radiation constant,  $m$  the mass of an electron,  $c$  the velocity of light and  $\phi$  the angle of scattering. In the present experiments  $\phi$  was made as large as possible ( $169^\circ$ ) by placing the slits and calcite crystal in a lead box fastened to the Coolidge tube. Mo  $K\alpha$  and  $K\beta$  radiation was scattered from paraffin back to the crystal and then to a photographic plate; Zr  $K\alpha$  rays for comparison were obtained from a Zr radiator. The best plate required an exposure of 48 hr. The change of wave-length was measured 16 times by means of a special microphotometer. After certain corrections were made, the shift came out  $(.04825 \pm .0002)\text{\AA}$ ; the theoretical value is  $.04798 \pm .0001$ . This agreement is an excellent confirmation of the theory. This effect may also be used to obtain a measurement of  $m$  which is independent of  $e/m$ . The value of the mass of the electron thus computed from these measurements is  $(8.99 \pm .034) \times 10^{-28}$  gm in agreement with the mean result from deflection experiments, whereas the spectroscopic value of  $e/m$  gives 9.04.

ACCORDING to the quantum theory, the change of wave-length of x-rays when scattered is given by the expression<sup>1</sup>

$$\delta\lambda = (h/mc) (1 - \cos \phi) \quad (1)$$

where  $h$  is Planck's radiation constant,  $m$  is the mass of the electron,  $c$  the velocity of light and  $\phi$  the angle which the scattered beam makes with the primary beam. Of the many published tests of this equation, the ones for which the greatest precision is claimed are perhaps those of A. H. Compton,<sup>2</sup> Becker and others<sup>3</sup> and Kallman and Mark.<sup>4</sup> Compton used an ionization spectrometer and a carbon radiator, and made tests at different angles of scattering. His probable error was about 2 percent. The others obtained photographic spectra of rays scattered at about

<sup>1</sup> A. H. Compton, Phys. Rev. 21, 207 and 483 (1923).

<sup>2</sup> A. H. Compton, Phys. Rev. 22, 409 (1923).

<sup>3</sup> J. A. Becker, E. C. Watson, W. R. Smythe, R. B. Brode and L. M. Mott-Smith, Phys. Rev. 23, 763 (1924).

<sup>4</sup> H. Kallman and H. Mark, Naturwissenschaften 13, 297 (1925).

90°, Becker using aluminum as radiator, and Kallman and Mark using graphite. In both of the latter investigations the estimated probable error was about 1 percent. Greater precision in testing the equation should be obtained if the angle of scattering is increased to nearly 180°, for then  $\delta\lambda$  is greater, and, since it is the cosine of the angle which enters into the equation, the error in the calculated value of  $\delta\lambda$  resulting from an error in measuring  $\phi$  is greatly reduced.

*Experimental procedure.* A test in which a large angle of scattering is used has been made with the apparatus shown diagrammatically in Fig. 1. X-rays from the molybdenum target  $T$  of an x-ray tube fall on a paraffin radiator  $R$ , and some of the rays are scattered almost directly back to the calcite crystal  $C$ . The slit which determines the width of the spectrum lines is at  $S$ , and the photographic film is placed beyond the lead

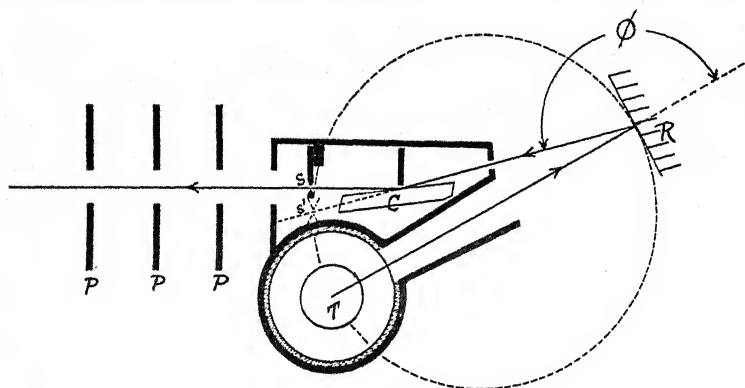


Fig. 1. Arrangement of apparatus.

screens  $P$ . The image  $S'$  of the slit  $S$  as reflected in the face of the crystal lies as close to the target  $T$  as is conveniently possible. It will be seen also from the figure that the angle of scattering  $TRS'$  varies but slightly as one alters the part of the radiator  $R$  from which the rays are scattered. This arrangement therefore affords a means of securing a spectrum of rays scattered at a nearly definite as well as a large angle.

The x-ray tube employed was of the narrow cylindrical, water-cooled type described by Compton.<sup>1</sup> It was allowed to rectify its own current of 18 to 20 m-amp., which was supplied by a transformer operating at about 40 peak kv. Surrounding the tube to eliminate stray x-rays was a cylindrical lead sleeve, insulated from the glass walls of the tube by about 1.2 mm of mica. In this sleeve there was an aperture to permit x-rays to proceed in the direction of the radiator. The crystal was set in plaster of Paris and the crystal and slit were supported in a frame rigidly attached to the lead sleeve and were enclosed by lead except as indicated in Fig. 1.

The distance from the target to the radiator was 10 cm. The slit was .4 mm wide and 2.2 cm long and the distance from the slit to the film was about 30 cm. . .

An enlargement of the best of several photographs thus obtained is reproduced in Fig. 2. The negative shows plainly the molybdenum  $K\alpha$  and  $\beta$  lines. This represents an exposure, using an intensifying screen, of 32 hours with a paraffin radiator and 16 hours with a zirconium

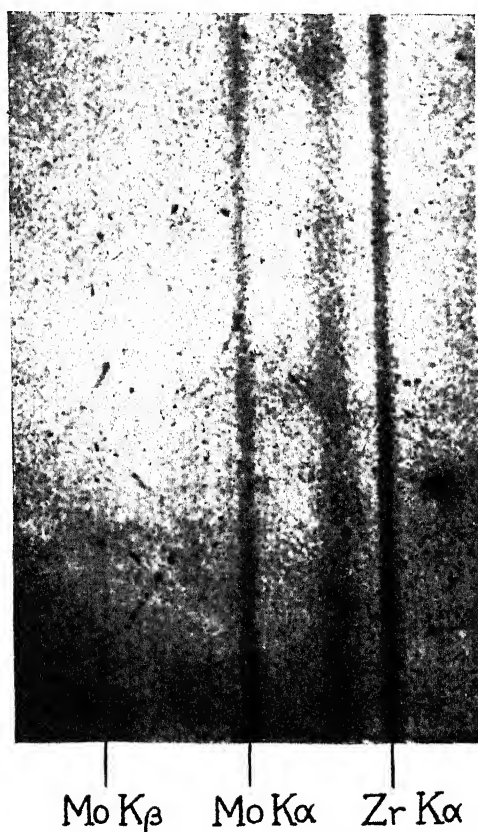


Fig. 2. Enlargement of the spectrogram of which the density distribution is given in Fig. 3.

radiator. Attempts to secure photographs in which the molybdenum  $K\beta$  modified and unmodified lines were strong enough to measure precisely were unsuccessful, due partly to the difficulty of making a tube operate under the conditions of the experiment with sufficient life to permit an exposure of the required length.

*Determination of  $\phi$ .* The angle  $\phi$  between a line joining the center of the focal spot and the radiator and a line from the radiator to the crystal,



was determined by a geometrical method to be  $169.7^\circ$ . As we have seen, the variation in  $\phi$  due to the fact that different portions of the scattered x-rays come from different portions of the radiator, is practically negligible; but there is a certain range of values of  $\phi$  which results from the length of the slit and the size of the target. Rays which pass through the end of the slit are scattered at a larger angle than those which pass through the center. The range of  $\phi$  due to the length of the slit was from  $167.7$  to  $169.7^\circ$ .

The target was photographed by allowing rays to pass through a pin-hole in a sheet of lead. From the size of the photograph and the distance of the film and target from the pin-hole, the size of the portion of the target from which x-rays proceeded was calculated. This was found to

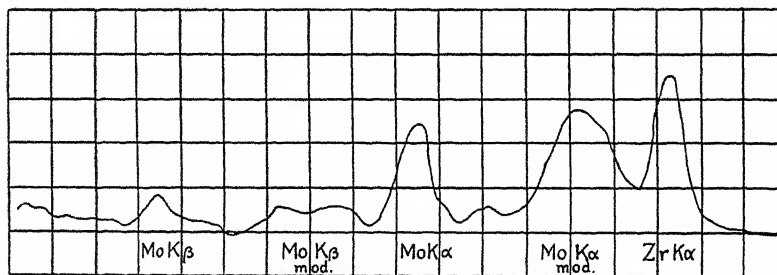


Fig. 3. Microphotometric measurement of the spectrogram reproduced in Fig. 2.

be .5 cm in the vertical direction. The center of the target was 1.6 cm below the image of the slit. The smallest distance from the target to the image of the slit was thus 1.35 cm, and the largest distance 1.85 cm. Taking this into account the range of  $\phi$  was from  $166.3$  to  $171.5^\circ$ .

*Measurement of  $\delta\lambda$ .* Measurements of  $\delta\lambda$  were made on the film shown in Fig. 2. For this purpose 16 curves for different portions of the film were made with a microphotometer which consisted of a Coblenz thermopile of about 20 elements connected with a Leeds and Northrup high sensitivity galvanometer. One of these curves is shown in Fig. 3. The position of each peak was determined by making several measurements of the middle of the upper tenth of the curve representing the spectrum line. If  $b$  is the measured distance in centimeters between the Mo K $\alpha$  peak and the Mo K $\alpha$  modified peak,  $a$  the distance between the Mo K $\alpha$  peak and the Zr K $\alpha$  peak, and  $\Delta$  the wave-length difference between the Mo K $\alpha_1$  and the Zr K $\alpha_1$  lines, the value of  $\delta\lambda$  is approximately

$$\delta\lambda = (b/a)\Delta \quad (2)$$



The value of  $\Delta$  according to the recent wave-length determinations of Leide,<sup>5</sup> is  $0.78429 - 0.70780 = 0.07649\text{\AA}$ .

In order to obtain a precise result the following small corrections were applied:

(a) On the Mo  $K\alpha$  peak: (1) For the effect of the  $\alpha_2$  line in shifting the peak, due mainly to the  $\alpha_1$  line. (2) For the effect of the Zr  $K\beta$  line in shifting the peak of the combined Mo  $K\alpha_1$  and Mo  $K\alpha_2$  line.

(b) On the Mo  $K\alpha$  modified peak: For the effect of the modified  $\alpha_2$  line.

(c) On the Zr  $K\alpha$  peak: (1) For the effect of the  $\alpha_2$  line in shifting the  $\alpha_1$  peak. (2) For the effect of the modified Mo  $K\alpha$  line in shifting the Zr  $K\alpha_1$  and  $K\alpha_2$  peak.

(d) A correction to change from the measurement of the angle to the measurement of the sine, since  $\lambda$  is proportional to  $\sin \theta$ .

The calculation of these corrections was facilitated by the observation that the photometer curve representing a simple spectrum line can be represented very approximately by an expression of the form  $y = y_0 e^{-x^2}$ . When these corrections are taken into account, the change of wave-length can be expressed as

$$\delta\lambda = (b/a) (.07658\text{\AA}) - .00040\text{\AA}. \quad (3)$$

This differs from the approximate relation (2) by only 0.7 percent. The average value of  $\delta\lambda$  thus obtained from 16 photometric curves is

$$\delta\lambda = (.04825 \pm .00017)\text{\AA}. \quad (\text{expt.})$$

In calculating  $\delta\lambda$  from Eq. (1), we may take  $1 - \cos \phi = 1.984 \pm .001$ . The value of  $h$  as determined by Duane, Palmer and Chi-Sun-Yeh<sup>6</sup> is  $(6.556 \pm .0009) \times 10^{-27}$  erg sec.  $m$  is given by the expression  $m = e/(e/m)$ , where for  $e$  we may use Millikan's<sup>7</sup> value of  $(4.774 \pm .005) \times 10^{-10}$  e.s.u., and for  $e/m$  Babcock's<sup>8</sup> value  $(1.761 \pm .001) \times 10^7$  e.m.u. These values give

$$\delta\lambda = (.04798 \pm .00009)\text{\AA}, \quad (\text{theory})$$

This differs from the experimental value by an amount which is just within the combined probable error.

*Discussion.* This result is an excellent confirmation of the quantum formula for the change of wave-length of scattered x-rays.

<sup>5</sup> A. Leide, *Comptes Rendus* **180**, 1203 (1925).

<sup>6</sup> Duane, Palmer and Chi-Sun-Yeh, *Jour. Opt. Soc. Am.* **5**, 396 (1921).

<sup>7</sup> R. A. Millikan, *Phil. Mag.* (July, 1917).

<sup>8</sup> H. D. Babcock, *Astrophysical Jour.* **58**, 149 (1923).

If we write Eq. (1) in the form

$$m = h(1 - \cos \phi) / c\delta\lambda,$$

we see that a measurement of  $\delta\lambda$  affords a method of measuring the mass of the electron, which is independent of  $e/m$ . This is of especial interest in view of the fact that the spectroscopic values of  $e/m$  are consistently lower than those obtained by the deflection of streams of electrons.<sup>9</sup> Using for  $c$  the value  $2.9986 \times 10^{10}$  cm/sec and for  $h$ ,  $\delta\lambda$  and  $\phi$  the values given above,  $m$  is thus found to be  $(8.99 \pm .034) \times 10^{-28}$  gm. This value is probably not as accurate as the value  $(9.04 \pm .01) \times 10^{-28}$  gm based on Babcock's spectroscopic determinations of  $e/m$ ; but it is interesting to note that it lies closer to the value  $8.98 \times 10^{-28}$  gm calculated from Birge's average  $e/m = 1.773 \times 10^7$  e.m.u. based chiefly on deflection experiments.<sup>10</sup>

In conclusion the writer desires to express his appreciation of the continued encouragement given by Professor A. H. Compton, who suggested the problem and has directed the work on it, and to acknowledge his indebtedness to his friend Mr. Y. H. Woo for assistance in evacuating the x-ray tubes.

RYERSON LABORATORY,  
UNIVERSITY OF CHICAGO,  
Sept. 22, 1925.

<sup>9</sup> Cf. Babcock, loc. cit.<sup>8</sup>

<sup>10</sup> R. T. Birge, Phys. Rev. 14, 363 (1919).

THE DIRECTION OF EJECTION OF PHOTO-ELECTRONS  
PRODUCED BY X-RAYS

BY D. H. LOUGHRIDGE

## ABSTRACT

Stereoscopic photographs of photo-electrons produced by 40 kv Mo K $\alpha$  x-rays, were examined by a stereoscopic comparator which gave a quantitative measure of the initial direction of ejection in space. The measurement of twenty-four distinct tracks in a series of twenty-nine pairs of photographs showed that the most probable angle of ejection was about 70° with the primary beam. This supports the view that the electric vector of the radiation plays a very important part in the production of photo-electrons. The small forward or backward component, noticed in many tracks, must come from the random momentum of the electron in its orbit before ejection.

IT has been shown by Bothe<sup>1</sup> that the most probable direction of ejection of photo-electrons produced in various gases by x-rays of varying hardness, makes an angle between 80 and 85° with the primary beam. This varies slightly with the gas and with the hardness of the rays. P. Auger<sup>2</sup> has also reported similar results. However, C. T. R. Wilson observed three characteristic angles of ejection of photo-electrons in air, namely 45, 90, and 135° with the primary beam. The present experiment was performed in order to measure accurately the initial angles of ejection of photo-electrons in air produced by radiation of a definite frequency.

## EXPERIMENTAL PROCEDURE

Stereoscopic photographs were taken of the photo-electron tracks produced in moist air at atmospheric pressure by the K $\alpha$  radiation from molybdenum. The beam of x-rays (Fig. 1) from the molybdenum target of a water-cooled Coolidge tube, operated at about 40 kv and 35 m-amp., was sent horizontally through lead collimating slits and a zirconium oxide filter which gave practically homogeneous radiation. This beam passed through a Wilson cloud expansion chamber about 11 cm in diameter. An electric field of about 100 volts per cm was maintained, except when the picture was taken, between the top of the piston and the lower surface of the chamber top. The construction and assembly of the expansion chamber was similar to that described by C. T. R. Wilson.<sup>3</sup> An arc with

<sup>1</sup> Bothe, *Zeits. f. Phys.* **26**, 59-73 (1924).

<sup>2</sup> P. Auger, *Comptes Rendus* **178**, 929 (1924).

<sup>3</sup> C. T. R. Wilson, *Proc. Roy. Soc.* **104**, p. 1 (1923).

Sperry searchlight carbons, was used as a source of illumination. During adjustment of the apparatus it was operated at about 15 amp. but just before a picture was taken the current was increased to 100 amp. by short circuiting a series resistance. A shutter kept the light out of the chamber except when needed. This precaution was found necessary as even very slight heating effects within the chamber produced vortex motion of the gas which distorted the tracks. The illumination was sent in horizontally, by suitable condensing lenses, at right angles to the x-ray beam. The matched lenses were Tessar  $f/4.5$ , 5.5 cm focus and were mounted in a box camera with their centers 6.5 cm apart. A Graflex focal plane shutter which exposed the two plates simultaneously and was released by a plunger type solenoid, regulated the exposure. Eastman Speedway  $3\frac{1}{4} \times 4\frac{1}{4}$ " plates were used.

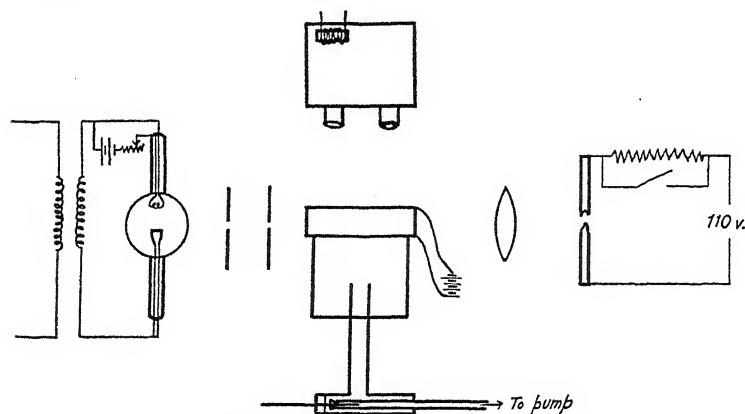


Fig. 1. Diagram of apparatus.

The timing was performed by two falling balls, released simultaneously by two solenoids in series; the first ball caused the expansion by opening the valve underneath the piston and the second ball, immediately afterward, closed the primary switch of the transformer operating the x-ray tube and then closed the circuit which operated the camera shutter. The adjustments on all these devices were regulated until sharp photographs were obtained. The switch, which controlled the solenoids holding the falling balls, also cut off the electrostatic field in the chamber.

### RESULTS

A series of 26 pairs of photographs were obtained using expansion ratios between 1.29 and 1.34. Some of these contained too many tracks for accurate measurement but, by cutting down the size of the x-ray beam, photographs were obtained where distinct photo-electron tracks

could be found which did not overlie any others and were sharply in focus. The depth in the photograph was obtained by using a stereocomparator and the height and breadth were measured directly on the plate by dividers. By thus obtaining the difference between the coordinates of the initial point of the track and point where the first bend occurred, the initial direction of ejection in space could be calculated. For the calculation of the depth in the picture the angle between the optic axes of the two lenses was needed, which was  $13^\circ$ .

Twenty-five distinct tracks were found in the series of photographs. In all of these there was no ambiguity as to which was the head of the track. Arranged in order of increasing angle between the primary beam and the initial part of the track, the values found are 21, 45, 48, 49, 52, 53, 59, 59, 67, 69, 70, 73, 74, 80, 84, 88, 90, 96, 99, 100, 104, 107, 119 and  $123^\circ$ . These values are plotted in Fig. 2, with angles as abscissas, and the number

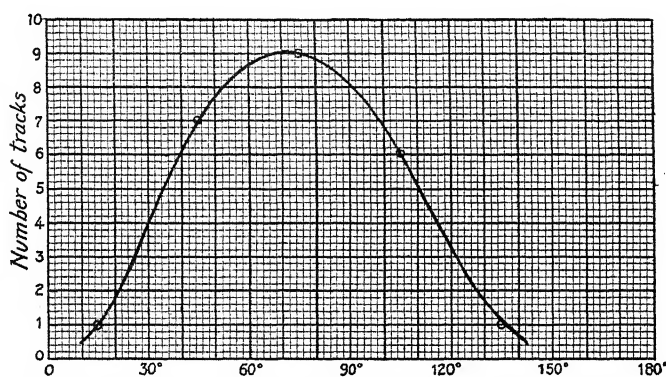


Fig. 2. Distribution of the directions of the 24 photo-electron tracks with respect to the x-ray beam.

of tracks starting within each  $30^\circ$  interval as ordinates. The curve clearly shows a marked angle of most probable emission around  $70^\circ$ . Practically the same maximum is obtained if the angular intervals chosen for plotting are  $10^\circ$ ,  $15^\circ$ ,  $45^\circ$ , or  $60^\circ$ ; but the number of data hardly justifies the smaller intervals while the larger intervals give too few points to insure a clear curve. It is felt that the  $30^\circ$  interval chosen shows the effect fairly and clearly. It should also be pointed out that tracks lying close to  $0^\circ$  or  $180^\circ$  with the primary beam, would be the easiest to measure as they would all lie more nearly in the plane of the plate, while the ones bunched around  $90^\circ$  would contain some lying perpendicular to the plane of the plates and would therefore be more difficult to see. Thus it is obvious that if there existed a random distribution of the directions of

ejection one would probably find more around  $0^\circ$  and  $180^\circ$  than around  $90^\circ$ .

This tendency for the emission at nearly right angles to the primary beam is in agreement with the view that the electric vector of the rays plays a very important part in the process. In fact, Bubb has shown<sup>4</sup> that when polarized x-rays are used the most probable direction of emission lies in the plane containing the electric vector.

The small forward component noticed in most of the tracks supports the view that the energy of the primary quanta is imparted to the photo-electron by a forward impulse along with the sidewise impulse of the electric vector.<sup>5</sup> Because of these two effects alone, on the basis of conservation of momentum, no tracks with backward components would be expected, but by combining with them the random momentum of the electron in its orbit, a backward momentum becomes possible.

I am grateful to Professor R. A. Millikan for his advice and inspiration during the progress of this work.

NORMAN BRIDGE LABORATORY,  
CALIFORNIA INSTITUTE OF TECHNOLOGY,  
PASADENA, CALIFORNIA.  
September 18, 1925.

<sup>4</sup> Bubb, *Phys. Rev.* 23, p. 137 (1924).

<sup>5</sup> Bubb, *Phil. Mag.* 49, p. 824 (1925).

# A REINVESTIGATION OF THE WAVE-LENGTHS AND RELATIVE INTENSITIES IN THE MOLYBDENUM K SERIES X-RAY SPECTRUM

By SAMUEL K. ALLISON<sup>1</sup> AND ALICE H. ARMSTRONG

## ABSTRACT

The x-ray beam from a water-cooled target of a tube carrying 25 m-amp. from a 50 kv storage battery, was limited to 2 minutes and reflected from a calcite crystal of a spectrometer with a Genevoise scale reading to 2 seconds, into an ionisation chamber. The 3rd to 5th orders were used. The angle of reflection for each wave-length was determined by readings on both sides of the direct beam. Corrections were applied for the temperature of the crystal above 18°, for the eccentricity of the scale and for refraction. *The wave-lengths* are found to be (taking  $d=3.028\text{\AA}$ ):  $a_2=.711835$ ,  $a_1=.707525$ ,  $\beta_3=.631354$ ,  $\beta_1=.630791$ ,  $\gamma=.619526$ . From 3 to 5 determinations were made for each line, the average deviation from the mean being .000025. The mean deviation from the last results of A. Leide is .00003 except for  $\beta_1$  for which his value seems too high. The separation  $\beta_3-\beta_1$  is .000563 in good agreement with the separation  $L\beta_3-L\beta_1$  determined by Coster. The wave-lengths taking  $d=3.02904\text{\AA}$  and the  $\nu/R$  and  $\sqrt{\nu}/R$  values for the K lines and for the corresponding energy levels in the Mo spectrum are also given. The K absorption limit was found at .61830A. *Relative intensities.* Assuming each component of the  $\beta$  doublet to be a single line of the same width, the relative intensities come out  $K\beta_1/\beta_3=2.0$ , in agreement with the theoretical predictions of Sommerfeld and of Coster and Goudsmit. In the case of the  $\beta$  and  $\gamma$  doublets the total intensity of each doublet was taken proportional to the area under it, correcting for the K absorption in the case of the  $\gamma$  peak. The relative intensities then come out  $K\beta/\gamma=7.7$ , which is greater than the corresponding ratio for tungsten, indicating a decrease with increasing atomic number.

## APPARATUS AND METHOD OF MEASURING WAVE-LENGTHS

THIS paper is a report of experiments carried out in the laboratory of Professor William Duane at Harvard University. We have re-measured the wave-lengths of the lines in the molybdenum K series spectrum, and have redetermined the relative intensities of some of the lines which are not widely separated in wave-length.

The apparatus available for this investigation had several advantages over that with which the previous work on the molybdenum spectrum in this laboratory was performed. (1) We had at our disposal an ionisation spectrometer with a Genevoise scale, on which settings could be made to 2 seconds of arc. (2) Tubes with water-cooled targets were employed which permitted the use of much more power than that used

<sup>1</sup> National Research Fellow.



in the previous work. (3) A new 50,000 volt high capacity storage battery made it possible to operate at higher voltages and currents for longer intervals than before.

The new storage battery and general arrangement of the apparatus have been described.<sup>2</sup> The spectrometer measurements were made by the ionisation method, as used previously in this laboratory. The position of the crystal was read on the accurate silver scale with a traveling microscope, and the ionisation chamber was set approximately by reading its position on a brass scale concentric with the silver scale. Approximate settings of the ionisation chamber were sufficient to follow the reflected beam since the slit in front of the chamber was quite wide (6-8 mm). All angular readings used in the calculation of wave-lengths were settings of the crystal table. The x-ray beam incident upon the crystal was limited by two slits 37 cm apart. The slits were of approximately the same width, and limited the angular breadth of the beam to about 2 minutes of arc. The vertical height of the beam was limited by a stop 1 cm high placed between the x-ray tube and the crystal 5 cm from the crystal.

In the experiments on the wave-lengths of lines, the x-ray tube was run at 25 milliamperes and a constant battery voltage of about 50 kilovolts. The ionisation currents were read on an electrometer and scale system whose sensitivity was about 3 meters per volt.

The wave-length measurements reported here were all obtained in higher orders of reflection from calcite. In the crystal used there was no good evidence of broadening of the lines in higher orders. In a determination of wave-length, the crystal was rotated in steps of 15 seconds each through the angular range in which the center of a line had been found to lie by previous trials. Two settings could thus be located at which the ionisation current was higher than for any other two in the vicinity, and from the relative intensities at these two settings the position of the line could be estimated within 2 or 3 seconds of arc.<sup>3</sup> The crystal table and ionisation chamber were then at once shifted so that the same wave-length was reflected from the crystal on the opposite side of the direct beam, and again the setting of the crystal for the center of the line was determined. The temperature was taken during each observation. The two determinations of angle were made as nearly simultaneously as possible because it was found that from day to day, from unknown causes, the position of the crystal at which maximum reflection in a line was obtained varied through an angular range which

<sup>2</sup> Armstrong and Stiffler, *J. Opt. Soc. Amer. and Rev. Sci. Inst.* **11**, 509 (1925).

<sup>3</sup> Cf J. C. Hudson, *J. Opt. Soc. Amer. and Rev. Sci. Inst.* **9**, 259 (1924).

in some cases was as large as a minute of arc. We have made determinations of angles of reflection in which the setting of the crystal was varied in steps of less than 15 seconds, but we believe that no additional accuracy is thereby gained.

In the measurement of the molybdenum K critical absorption wavelength, we used general radiation from a tube with a water-cooled copper target containing a button of tungsten. The absorbing substance was a screen of ammonium molybdate. The width of the beam in the absorption measurements was slightly over 4 minutes of arc. The angular measurements were made in the same way as those for line wave-lengths, except that the angular reading corresponding to an absorption wave-length is that of a point on the discontinuity half way between the base-lines of the radiation of shorter and longer wave-lengths.

#### CORRECTIONS AND SOURCES OF ERROR

It is well known that in this method of measurement, in which the wave-lengths are calculated from angular settings of the crystal, the penetration of the rays into the crystal before reflection introduces no error. Since, also, the face of the crystal may be considered plane, no appreciable error is introduced if the point of effective reflection of the beam does not lie exactly in the axis of rotation of the spectrometer. In our experiments the method of making the point of effective reflection coincide approximately with the axis of rotation of the spectrometer was to limit by a narrow slit the beam entering the ionisation chamber, and then to vary the position of the crystal and other slits until the angle through which the ionisation chamber was turned to obtain maximum intensity for the beam reflected from the crystal was just twice the angle traversed by the crystal over a large range.

If the sleeve which carries the microscopes and crystal does not rotate about the same vertical axis as that which carries the scale, the angle as read on the scale by one microscope will not be the true angle between the two settings of the crystal. The true angle may be ascertained by reading two microscopes, *A* and *B*, at each setting. *A* and *B* on our instrument are very nearly 180° apart. The true angle through which the crystal is turned is the average of the apparent angles as read on *A* and *B*. Before measuring the wave-lengths of the molybdenum lines, we determined the correction to be applied to the scale in the region in which angular settings would be taken. We found that a correction of 6 seconds should be added to the apparent angle (35° to 70°) as read on microscope *A*. The eccentricity, of course, varied somewhat with the settings, but the variations were well within the limit of error of locating the

peaks, and we have corrected all readings on microscope *A* in this range by 6 seconds. In the measurement of the wave-lengths of lines, all settings were made with vernier *A* alone. This technique is probably not the best, as it is known that the eccentricity varies somewhat with temperature and other factors; therefore it would be advisable to read both microscopes for every wave-length determination. After the wave-lengths had been measured, we redetermined the eccentricity in the same part of the scale as before and found that it was not the same, but that the variations were well below the error in locating the positions of the lines themselves.

In the measurement of the critical absorption wave-length, the apparatus was slightly modified so as to permit the reading of both microscopes at once. The readings were taken in a different part of the scale, in which the eccentricity correction to be applied to *A* was only two seconds.

The observed wave-lengths were corrected for the temperature of the crystal from the table in Siegbahn's "Spektroskopie der Röntgenstrahlen," p. 87. All corrections were made to a temperature of 18°C.

It is now known that a correction must be applied to the wave-length calculated by the simple Bragg law on account of the fact that the index of refraction of the crystal for the x-rays becomes appreciable when precision measurements are made. The true wave-length in air may be obtained by the formula<sup>4</sup>

$$n\lambda = 2d \sin \theta (1 - \delta / \sin^2 \theta) \quad (1)$$

where  $\lambda$  is the true wave-length in air,  $d$  is the grating space,  $\theta$  is the observed glancing angle, and  $\delta = 1 - \mu$ , where  $\mu$  is the index of refraction of the crystal for the x-rays. Hatley<sup>5</sup> has adopted a suggestion of Bergen Davis and by an ingenious method obtained a measurement of the index of refraction of calcite for Mo  $K\alpha_1$  x-rays. The value given by Hatley for  $\delta$  is  $2.03 \times 10^{-6}$ , which agrees well with that calculated by the Lorentz dispersion formula. In the higher orders of reflection, where  $\theta$  is large, it may be seen from Eq. (1) that the deviation from the Bragg law is very slight. In the first order it is about  $-.0001A$  for Mo  $K\alpha_1$  from calcite. We have neglected the change of index of refraction with wave-length throughout the molybdenum spectrum. We have instead based our calculations on the value given by Hatley, and have used for  $\theta$  an angle lying between the critical angles for Mo  $K\beta$  and Mo  $K\alpha$ . The extent of the correction applied is shown in the tables.

<sup>4</sup> A. H. Compton, *Phil. Mag.* **45**, 1121 (1923)

<sup>5</sup> C. C. Hatley, *Phys. Rev.* **24**, 486 (1924).

A possible source of error of unknown magnitude lies in the ruling of the scale of the instrument itself. It is quite possible that certain regular variations may recur in the rulings of these scales; through intervals of a degree or so five minute marks may be one or two seconds displaced. It seems unlikely that in the large angles measured such a periodic variation would introduce appreciable error. No calibration of the scale of our instrument has been attempted; accordingly our measurements are subject to such errors as may occur in the scale itself.

#### METHOD OF CALCULATION OF WAVE-LENGTH

Different investigators are not yet agreed on the proper value of  $d$  for calcite. Recently A. H. Compton, O. K. DeFoe, and H. N. Beets<sup>6</sup> have redetermined the density and rhombohedral angle of calcite, and have recommended for  $d$  the value used by Siegbahn in the calculation of his results, namely  $3.02904 \times 10^{-8}$  cm at  $18^\circ\text{C}$ . The wave-lengths previously measured in this laboratory and some determined by Bergen Davis and his collaborators have been calculated on the basis  $d = 3.028 \times 10^{-8}$  cm at  $18^\circ\text{C}$ . There seems to be some ground for the opinion that higher values of density should be given more weight than lower values in the averaging of a series of determinations. If this is true, then lower values of  $d$  are more likely to be correct. The wave-lengths reported here are given both on the basis  $d = 3.028\text{\AA}$  and on  $d = 3.02904\text{\AA}$  at  $18^\circ\text{C}$ .

Compton and his collaborators report that in their measurements of the densities of representative samples of calcite differences in density greater than the experimental error occur. This at once raises the question of the generality of wave-length determinations based on crystalline diffraction. It seems highly probable that the precision measurements of wave-length now possible should be found to depend on the particular calcite crystal used, on account of the varying composition of calcite. The varying amounts of impurity in calcite may be a source of the discrepancies found in the wave-length determinations by different investigators. We know nothing of the previous history of the sample of calcite which we used. It is a small, clear, museum specimen which was found by trial to give sharp lines in higher orders of reflection.

The method employed in the calculation of the wave-length in air at  $18^\circ\text{C}$  from the observed angle was as follows. From the observed glancing angle a preliminary wave-length was calculated on the basis  $d = 3.028\text{\AA}$ . This preliminary wave-length was then corrected to  $18^\circ\text{C}$ ; this correction was in general a small positive one, since the temperatures were usually above  $18^\circ\text{C}$ . After a number of these corrected preliminary

<sup>6</sup> Compton, DeFoe and Beets, *Phys. Rev.* **25**, 618-629 (1925).

wave-lengths had been obtained in the same order of reflection, they were weighted as to reliability and averaged. The true wave-length in air was obtained by correcting the order average for refraction. The temperature corrections were very small, as were also, on account of high order, those for refraction.

TABLE I

*Wave-lengths of Mo K series lines.*

Wave-lengths in this table are in angstroms and have been calculated on the basis  $d(18^\circ) = 3.028\text{\AA}$ .

	Order	Date	$\lambda$ at $18^\circ\text{C}$	Wt.	av. $\lambda$ for order	Corr. for refraction	$\lambda$ in air at $18^\circ\text{C}$	Wt.	Final $\lambda$
$K\alpha_2$	Third	Mar. 23	.711789	(1)	.711789	-.000012	.711777	(1)	
	Fourth	Mar. 26	.711834	(1)					
		Mar. 26	.711670	(0)					
		Mar. 27	.711897	(1)					
		Mar. 27	.711834	(1)					
		Mar. 27	.711862	(1)	.711857	-.000007	.711850	(4)	.711835
$K\alpha_1$	Third	Feb. 26	.707558	(1)					
		Mar. 21	.707590	(1)					
		Mar. 23	.707577	(1)	.707575	-.000012	.707563	(3)	
	Fourth	Mar. 21	.707535	(1)					
		Mar. 23	.707534	(1)					
		Mar. 24	.707484	(1)	.707518	-.000007	.707511	(3)	
	Fifth	Mar. 24	.707453	(1)					
		Mar. 24	.707532	(1)					
		Mar. 24	.707532	(1)	.707506	-.000004	.707502	(3)	.707525
$K\beta_1$	Fourth	Mar. 5	.630778	(1)					
		Mar. 7	.630801	(1)	.630790	-.000007	.630783	(2)	
	Fifth	Mar. 12	.630852	(1)					
		Mar. 17	.630772	(1)					
		Mar. 17	.630776	(1)	.630800	-.000004	.630796	(3)	.630791
$K\gamma$	Fourth	Mar. 13	.619543	(1)					
		Mar. 14	.619513	(1)					
		Mar. 17	.619543	(1)	.619533	-.000007	.619526		.619526
$K_{\text{abs}}$	Third	May 2	.61848	(1)					
		June 8	.61802	(3)					
		June 8	.61832	(1)					
		June 8	.61828	(1)	.61831	-.00001	.61830		.61830

The later steps of the calculation are shown in Table I. Each of these determinations is an absolute measurement in the sense that  $2\theta$  was measured directly. All the wave-length determinations which were made are included in the table. One-measurement of  $K\alpha_2$  gave a value so far from the mean of the others that we have not included it in the average and have weighted it zero.

In the fourth and, especially, the fifth orders, we obtained a good separation of the Mo  $K\beta$  doublet. This was announced in a preliminary

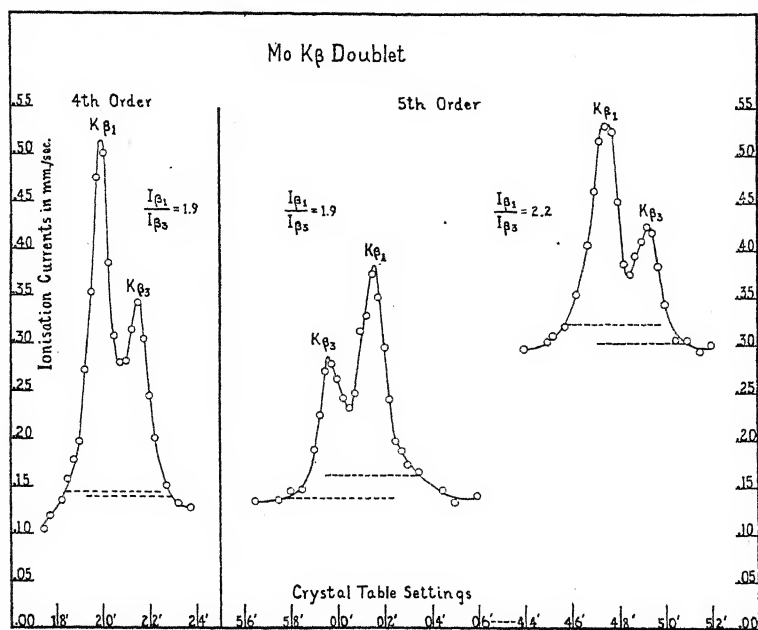


Fig. 1. Separation of Mo  $K\beta$  doublet.

report.<sup>7</sup> Some of the curves obtained are shown in Fig. 1 and the results in Table II. The doublet nature of this line has been experimentally

TABLE II

*Separation of Mo  $K\beta$  doublet and wave-length of Mo  $K\beta_3$ .*  
Wave-lengths in this table are in angstroms and have been calculated on the basis  $d(18^\circ) = 3.028$  Å.

Order	Date	Separation	Wt.	$\Delta\lambda$	Average	Final $\Delta\lambda$	Mo $K\beta_3$
Fourth	Mar. 10	1'22'' (L)	(1)	.000545			
	Mar. 7	1'31'' (R)	(1)	.000606	.000576		
Fifth	Mar. 10	1'56'' (L)	(1)	.000580			
	Mar. 12	1'44'' (R)	(1)	.000520	.000550	.000563	.631354

observed in Mo and other elements by various authors.<sup>8</sup> According to the accepted energy level diagram the same frequency difference should

<sup>7</sup> Allison and Armstrong, Phys. Rev. **25**, 882 (1925).

<sup>8</sup> M. de Broglie, Compt. Rend. **170**, 1053 and 1245 (1920).

Duane and Patterson, Bull. Nat. Res. Council. Vol. 1, Part 6, p. 393 (1920).

C. B. Croft, Phys. Rev. **24**, 9 (1924).

A. Leide, Compt. Rend. **180**, 1203 (1925).



appear between the lines  $L\beta_3$  and  $L\beta_4$ . Coster<sup>9</sup> has measured the wave-lengths of Mo  $L\beta_3$  and Mo  $L\beta_4$  and has found for the wave-lengths 5.0002 and 5.0358Å respectively. From these values it may be calculated that the wave-length difference in the  $K\beta$  doublet should be .000564Å. Our observed value of .000563Å agrees closely with this. The separation of .00039Å reported by Leide<sup>8</sup> agrees less well with the measurements of Coster in the L series.

TABLE III

Wave-length,  $\nu/R$ , and  $\sqrt{\nu/R}$  values for Mo K spectrum.

Line	$\lambda$		$\nu/R$		$\sqrt{\nu/R}$	
	$d=3.028\text{Å}$	$d=3.02904$	$d=3.028$	$d=3.02904$	$d=3.028$	$d=3.02904$
$K\alpha_2$	.711835Å	.712078	1280.17	1279.73	35.7795	35.7734
$K\alpha_1$	.707525	.707768	1287.97	1287.53	35.8882	35.8821
$K\beta_3$	.631354	.631571	1443.36	1442.86	37.9915	35.9850
$K\beta_1$	.630791	.631009	1444.65	1444.15	38.0085	38.0020
$K\gamma$	.619526	.619737	1470.91	1470.41	38.3525	38.3460
$K_{abs}$	.61830	.61851	1473.83	1473.33	38.391	38.384

Table III contains a summary of the wave-length values and the  $\nu/R$  ( $R=109737$ ) and  $\sqrt{\nu/R}$  values calculated from them. Table IV contains some of the energy levels which can be computed from the observed values in the K series by means of the combination principle.

TABLE IV

Energy levels in the Mo spectrum.

Level	$\nu/R$		$\sqrt{\nu/R}$	
	$d=3.028\text{Å}$	$d=3.02904$	$d=3.028$	$d=3.02904$
$K_{11}=K_{abs}$	1473.83	1473.33	38.395	38.384
$L_{21}=K_{11}-K\alpha_2$	193.66	193.60	13.916	13.914
$L_{22}=K_{11}-K\alpha_1$	185.86	185.80	13.633	13.631
$M_{21}=K_{11}-K\beta_3$	30.47	30.47	5.520	5.520
$M_{22}=K_{11}-K\beta_1$	29.19	29.18	5.403	5.402
$N_{21}N_{22}=K_{11}-K\gamma$	2.92	2.92	1.71	1.71

In Table V we have given the results of other investigators who have measured the wave-lengths of the Mo K series. The values given by C. C. Hatley and by R. von Nardroff are corrected for index of refraction but apparently not for temperature of the crystal. As far as we know, these corrections have not been applied to the other previous measurements which we have listed. The later measurements of Leide agree well with the ones reported here, except for the line  $K\beta_1$ . In addi-

<sup>9</sup> D. Coster, Phil. Mag. 43, 1070 (1922).



tion to the lines listed in Table V, Leide has reported a new line  $\beta_4$  which he attributes to the transitions  $\overline{O_{21}O_{22}} \rightarrow K_{11}$ . One of us<sup>10</sup> has commented on this reported line, which should lie between  $K\gamma$  and the absorption limit. According to the prevalent electron distribution schemes, such a line would probably be semi-optical. The corresponding transition

TABLE V

*Comparison of results of different investigations of the wave-lengths of the Mo K series lines.*

		$K\alpha_2$	$K\alpha_1$	$K\beta_3$	$K\beta_1$	$K\gamma$	$K_{abs}$
Duane and Patterson <sup>8</sup> (1920)	( $d=3.028$ )	.71212A	.70783		.63110	.6197	.61842
Overn <sup>11</sup> (1921)	( $d_{NaCl}=2.814$ )	.7131	.7087		.6324	.6268	.6214
Leide(1) <sup>12</sup>	( $d=3.02904$ )	.71187	.70759		.63075	.61927	....
Hatley <sup>5</sup> (1924)	( $d=3.028$ )	....	.707717		....	....	....
von Nardroff <sup>13</sup> (1924)	( $d=3.028$ )	....	....		.63102	....	....
Leide(2) <sup>14</sup> (1925)	( $d=3.02904$ )	.71208	.70780	.63163	.63124	.61969	....
Present results	( $d=3.028$ )	.711835	.707525	.631354	.630791	.619526	.61830
	( $d=3.02904$ )	.712078	.707768	.631571	.631009	.619737	.61851

in the L series ( $L\gamma_4$ ) has not been observed in molybdenum.<sup>9</sup> In a photograph it might well be difficult to distinguish this line from the Mo K critical absorption which occurs on account of the absorption of the target for its own radiation. We have not observed this line, though we have taken readings in the fourth order through the region in which it should occur.\*

#### RELATIVE INTENSITIES OF THE LINES

It is now well known from the researches of Duane and Stenström, Duane and Patterson, and Siegbahn and Žáček,<sup>15</sup> that the relative intensity of the components of the  $K\alpha$  doublet is 2/1 for a wide range of

<sup>10</sup> S. K. Allison, *Nature* **115**, 978 (1925).

<sup>11</sup> O. B. Overn, *Phys. Rev.* **18**, 350 (1921).

<sup>12</sup> A. Leide (1), Siegbahn, "Spektroskopie der Röntgenstrahlen," p. 102.

<sup>13</sup> R. von Nardroff, *Phys. Rev.* **24**, 143 (1924).

<sup>14</sup> A. Leide (2), loc. cit.<sup>8</sup>

\* *Note added to proof.* In a later publication (Thesis, Lund 1925) Leide no longer assigns this line (.61825A) to the transition  $\overline{O_{21}O_{22}} \rightarrow K_{11}$ , stating that it probably results from a forbidden jump from the levels  $N_{IV}N_V$ . From photometer curves of the photographs taken by him it appears improbable that the presence of this line can be ascribed to a misinterpretation of the K critical absorption from the target.

<sup>15</sup> These results are summarized in Siegbahn, *Spektroskopie der Röntgenstrahlen*, p. 97.

elements. We have not attempted any experiments expressly designed to confirm this fact for molybdenum.

In our investigation of the Mo  $K\beta$  doublet we have been able to measure the relative intensities of  $K\beta_1$  and  $K\beta_3$ , and we find, within the limit of experimental error, the ratio 2/1 for  $\beta_1/\beta_3$ . M. de Broglie noted in his first measurement of the doublet that the component of longer wave-length was the one of lesser intensity, and our work confirms this observation. The very small difference in wave-length between the components makes corrections for differential absorption by the walls of the tube, etc., unnecessary. Since, however, the doublet is not completely separated even in the fifth order, it is essential to make some assumptions concerning the base-line under each peak. In the first place, we have assumed that each component of the doublet is itself a single line, and that both components have the same intrinsic wave-length breadth. In this case, then, it is permissible to take the ordinate from the tip of the peak to the radiation under the tip (from other sources) as proportional to the intensity of the component. In addition we have assumed that the peaks representing the components are symmetrical about the ordinates determined by their tips. Then, if the separation of the doublet is  $\Delta\lambda$ , we may take the radiation at a point corresponding to  $\lambda\beta_1 - \Delta\lambda$  as the base-line for  $K\beta_3$ . This will include the general radiation under  $K\beta_3$  and, by the symmetry assumption, also the amount of  $K\beta_1$  which, because of incomplete resolution, is under the tip of  $K\beta_3$ . In the same way the radiation at  $\lambda\beta_3 + \Delta\lambda$  may be used as the base-line for  $K\beta_1$ . The base-lines given by this method are shown as dotted lines in Fig. 1. The method can be applied only when the resolution is great enough so that there is no appreciable radiation from  $\beta_1$  at  $\lambda\beta_3 + \Delta\lambda$  and vice versa. The results of three of the most trustworthy measurements are given in Fig. 1 and Table VI.

TABLE VI  
*Relative intensity of the lines Mo  $K\beta_1$  and  $K\beta_3$ .*

Date	Order	Ratio $\beta_1/\beta_3$	Wt.	Average
Mar. 7	4	1.9	(1)	
Mar. 10	5	1.9	(1)	
Mar. 12	5	2.2	(1)	2.0

Duane and Patterson<sup>16</sup> have measured the relative intensity of Mo  $K\beta$  to Mo  $K\gamma$  in the first and second orders and have found 6.3 and 5.5 respectively. They obtained this ratio from the highest points on the two peaks. Although this method is sufficient for a first approximation,

<sup>16</sup> Duane and Patterson, Phys. Rev. 19, 542 (1922); also, Proc. Nat. Acad. Sci. 8, 85 (1922).

a better procedure is probably to consider the *area* under each peak, since  $\beta$  and  $\gamma$  are both undoubtedly doublets of unequal wave-length separation. We have therefore taken the area under each peak above the general radiation as proportional to its intensity. The area was measured by means of an integrator. A typical curve showing  $\beta$  and  $\gamma$  is given in Fig. 2. The slits limiting the beam incident upon the crystal were somewhat wider than those used for wave-length measurements. In these experiments on the  $\beta$  and  $\gamma$  relative intensities, the x-ray tube had a

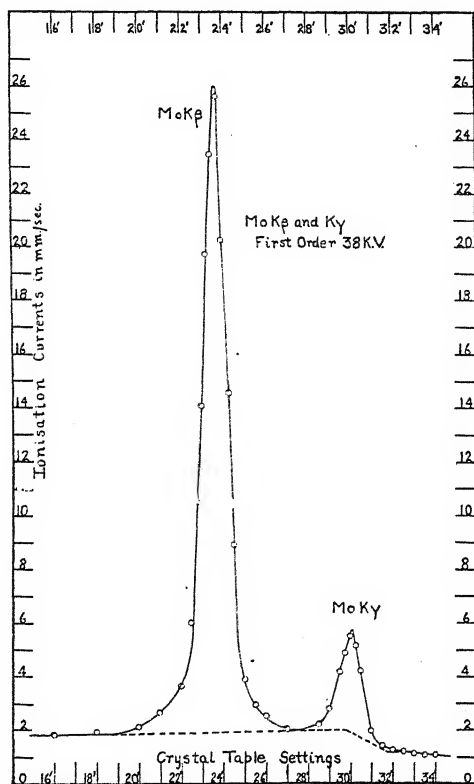


Fig. 2. Relative intensity of Mo  $K\beta$  and  $K\gamma$ .

thin blown-glass window to reduce absorption, and the x-rays entered the ionisation chamber through a mica window .002 cm. thick. The presence of absorption by the target itself is shown by the lower baseline on the short wave-length side of  $\gamma$ . On the assumptions that the center of the critical absorption rise lies 45 seconds to the short wave length side of  $\gamma$ , and that the breadth of the beam is equal to the breadth of the peak, we have drawn in the discontinuity as it must exist in the general radiation and have thus corrected the area of  $K\gamma$ . The critical

absorption and base-line are shown in dotted lines in Fig. 2. The results of several measurements of the relative intensity of  $K\beta$  to  $K\gamma$  are given in Table VII. In these determinations the voltage on the tube and the current through the tube were varied through rather wide limits, but no effect on the relative intensities of the lines could be detected. The relative intensities given are uncorrected for ordinary absorption effects.

TABLE VII

*Relative intensity of the lines Mo  $K\beta$  and  $K\gamma$ .*

Date	Order	Ratio $\beta/\gamma$	Wt	Average
Mar. 30	1	7.3	(1)	
Mar. 30	1	8.5	(1)	
Mar. 31	1	8.3	(1)	
Apr. 2	1	8.4	(1)	
Apr. 4	1	6.6	(1)	
Apr. 4	1	7.3	(1)	7.7

The relative intensity of  $K\alpha$  to  $K\beta$  has been measured for some elements in this region by Unnewehr<sup>17</sup> and by Siegbahn and Žáček.<sup>18</sup> We have not succeeded in obtaining a satisfactory value of this ratio for Mo because of the large correction for absorption which must enter.

#### DISCUSSION OF THE INTENSITY RESULTS

Recently Sommerfeld<sup>19</sup> and Coster and Goudsmit<sup>20</sup> have made theoretical predictions of the relative intensities of some doublets and "compound doublets" in x-ray spectra. They have based their predictions on the results of Burger and Dorgelo,<sup>21</sup> who have measured relative intensities in the optical region.

These investigators have found that the relative intensity of the components of the doublets in the principal series ( $1s-m_p$ ) of the alkalis is  $2/1$ . The well-known analogy of the x-ray levels to the optical levels of the alkalis would thus lead us to expect that the doublets of the K series would have the same relative intensity,  $2/1$ . By this analogy the  $K\beta$  doublet should correspond to the second member of the principal series ( $1s-3p_2, 3p_1$ ). The experimental intensity ratio reported here confirms the theoretical predictions of Sommerfeld and Coster and Goudsmit. It is also interesting to see that this simple ratio holds even though in falling from the M group to the K group the electrons pre-

<sup>17</sup> E. C. Unnewehr, Phys. Rev. **22**, 529 (1923).

<sup>18</sup> Siegbahn and Žáček, Ann. der Physik **71**, 187 (1923).

<sup>19</sup> A. Sommerfeld, Ann. der Physik **76**, 284 (1925).

<sup>20</sup> D. Coster and S. Goudsmit, Naturwissenschaften **1**, 11 (1925).

<sup>21</sup> Burger and Dorgelo, Zeits. f. Physik **23**, 258 (1924), etc.

sumably pass through the L group. Evidently in this case, at least, the relative intensity is not affected by the intervening group.

No quantitative theory has yet been devised to deal with the relative intensities of such lines as Mo  $K\beta$  and  $K\gamma$ .<sup>22</sup> Duane and Stenström<sup>23</sup> have measured the relative intensity of  $\beta$  to  $\gamma$  in the K series spectrum of tungsten and find 35/15 or 2.3/1. The observed ratio 7.7/1 in molybdenum shows that the  $\gamma$  line grows weaker as the atomic number of the radiating element decreases.

Our thanks are due Professor William Duane for his constant interest in this research.

CRUFT HIGH TENSION ELECTRICAL LABORATORY,  
HARVARD UNIVERSITY,  
August 11, 1925.

<sup>22</sup> *Note added to proof.* Our attention has been called to the paper of F. C. Hoyt (Phil. Mag. 46, 135, 1923) (see also article in this issue) in which an attempt was made to calculate the relative intensity of lines of this type by application of Bohr's correspondence principle. A dependence of the relative intensity on the atomic number may be inferred from considerations advanced in this paper.

<sup>23</sup> Duane and Stenström, Proc. Nat. Acad. Sci. 6, 477 (1920).

# EXPERIMENTS ON THE RELATIVE INTENSITIES OF SOME X-RAY LINES IN THE L SPECTRUM OF TUNGSTEN AND THE K SPECTRUM OF COPPER

BY SAMUEL K. ALLISON<sup>1</sup> AND ALICE H. ARMSTRONG

## ABSTRACT

**Tungsten L series lines.**—The experiments of Duane and Patterson on the strong lines in the L series of tungsten were repeated with improved apparatus, and also some of the weaker lines were studied. The value 10 obtained by Duane and Patterson for the relative intensity of  $La_1$  to  $La_2$  was confirmed. The theoretical ratio is 9. For the  $\beta$  group the *relative intensities* were found to be,  $\beta_1 : \beta_2 : \beta_3 : \beta_4 : \beta_5 : \beta_6 : \beta_7 : \beta_8 : \beta_9 : \beta_{10} = 100 : 49.3 : 15.0 : 7.7 : .47 : 2.0 : .4 : .68 : .60$ . The relative intensities of the weak lines among themselves are not very reliable on account of the faintness of the lines and the critical absorption of the target, yet it is clear that the forbidden lines  $\beta_9, \beta_{10}$  are of the same order of intensity as  $\beta_5, \beta_7$ . For the  $\gamma$  group the relative intensities were found to be,  $\gamma_1 : \gamma_2 : \gamma_3 : \gamma_4 : \gamma_5 : \gamma_6 : \gamma_8 = 100 : 14.0 : 22.3 : 7.0 : 3.0 : 2.3 : 1(?)$ .  $\gamma_8$  could not always be obtained. The determination of the intensity ratios for  $\alpha_1, \beta_1$  and  $\beta_2, \gamma_1$  was complicated by absorption in the target. The agreement of the observed value of the intensity ratio for  $\beta_3/\beta_4$  with the theoretical value 2, tends to confirm Stoner's suggestion that there are twice as many electrons in the  $M_{22}$  orbit as in the  $M_{21}$ . The deviation of the observed intensity ratio for  $\gamma_6/\gamma_2$  from 2 may be due to the influence of intervening levels.

**Copper K series lines.**—The average of two determinations of the *relative intensity* of  $\beta$  to  $\gamma$  gave 100/2.4. No reliable evidence of the non-diagram lines  $K\alpha_2\alpha_4$  was obtained at 30,700 volts.

THE experiments of Duane and Stenström<sup>2</sup> on the K series of tungsten and of Duane and Patterson<sup>3</sup> on the L series of tungsten and the K series of molybdenum furnish the first precision measurements of relative intensities of x-ray lines by the ionisation method; although the relative intensities of the K series lines of rhodium are shown in curves published still earlier by Duane and Hu<sup>4</sup> in their study of absorption and emission frequencies.

This problem of the relative intensities of x-ray lines has received a fresh impetus from the work of Ornstein, Burger, and Dorgelo on the relative intensities in the optical region.<sup>5</sup> These investigators have

<sup>1</sup> National Research Fellow.

<sup>2</sup> Duane and Stenström, Proc. Nat. Acad. Sci. 6, 477 (1920).

<sup>3</sup> Duane and Patterson, Proc. Nat. Acad. Sci. 6, 518 (1920); *ibid* 8, 85 (1922).

<sup>4</sup> Duane and Hu, Phys. Rev. 14, 369 (1919).

<sup>5</sup> Burger and Dorgelo, Zeits. f. Physik 23, 258 (1924); etc.;

Ornstein and Burger, Zeits. f. Physik 24, 41 (1924); etc.

found that the relative intensities of lines in multiplets are expressible in terms of whole numbers and are related to the inner quantum numbers of the states involved by the so-called "sum rules."

A. Sommerfeld<sup>6</sup> and also Coster and Goudsmit,<sup>7</sup> using the well-known optical analogy of the x-ray levels as a guide, have extended the results of Burger and Dorgelo to the region of x-ray spectra. Some of the theoretical relative intensities in the K and L series obtained by this method are shown in Table I.

TABLE I

*Theoretical relative intensities resulting from the extension of the rules of Burger and Dorgelo to x-ray spectra.†*

	Lines	Optical analogy	Relative intensity
K series	$\alpha_1 : \alpha_2$	$1s-2p_2, 2p_1$	2 : 1
	$\beta_1 : \beta_3$	$1s-3p_2, 3p_1$	2 : 1
	$\gamma$ -doublet	$1s-4p_2, 4p_1$	2 : 1
L series	$\beta_3 : \beta_4$	$2s-3p_2, 3p_1$	2 : 1
	$\gamma_3 : \gamma_2$	$2s-4p_2, 4p_1$	2 : 1
	$\gamma_4$ -doublet	$2s-5p_2, 5p_1$	2 : 1
	$l : \eta$	$2p_2, 2p_1-3s$	2 : 1
	$\beta_6 : \gamma_5$	$2p_2, 2p_1-4s$	2 : 1
	$\beta_7 : \gamma_8$	$2p_1, 2p_1-5s$	2 : 1
	$\alpha_1 : \alpha_2 : \beta_1$	$2p_2, 2p_1-3d_3, 3d_2$	9 : 1 : 5
	$\beta_2 : \beta_{15} : \gamma_1^*$	$2p_2, 2p_1-4d_3, 4d_2$	9 : 1 : 5
	$\beta_5 : \beta_{16} : \gamma_6^*$	$2p_2, 2p_1-5d_3, 5d_2$	9 : 1 : 5

† The notation is that recommended by Sommerfeld in the 4th edition of "Atombau und Spektrallinien."

\* The wave-lengths of  $\beta_{15}$  ( $N_{32} \rightarrow L_{22}$ ) and  $\beta_{16}$  ( $O_{32} \rightarrow L_{22}$ ) were measured and the lines named by Crofutt (Phys. Rev. 24, 9, 1924).

In the K series it is well known that the relative intensity of  $K\alpha_1/K\alpha_2$  is 2/1, as predicted in Table I. This ratio has been verified for a wide range of elements by the researches of Siegbahn and Žáček<sup>8</sup> and those of Duane and Stenström and Duane and Patterson referred to above. We have recently found<sup>9</sup> that the relative intensity of the components of the  $K\beta$  doublet is also 2/1, as predicted. Since the  $K\gamma$  doublet has not yet been separated, we cannot experimentally test the theoretical predictions in this case.

Unfortunately, only a few of the relative intensities predicted in the L series are suitable for experimental verification. With the exception of the combinations  $\beta_3\beta_4$ ,  $\gamma_3\gamma_2$ ,  $\alpha_1\alpha_2$ , and possibly  $\beta_2\beta_{15}$ , the lines in

<sup>6</sup> A. Sommerfeld, Ann. der Physik 76, 284 (1925).

<sup>7</sup> Coster and Goudsmit, Naturwissenschaften 1, 11 (1925).

<sup>8</sup> Siegbahn and Žáček, Ann. der Physik 71, 187 (1923).

<sup>9</sup> Allison and Armstrong, Phys. Rev. 25, 882 (1925); also preceding paper in this issue.



question are too far separated in wave-length or too weak to be measured at present.

The only previous measurements of relative intensities of lines in the L series, other than the qualitative visual estimation of photographic negatives, are those of Duane and Patterson<sup>3</sup> on the L series of tungsten. The results obtained by them are given in Table II. Sommerfeld<sup>6</sup> and Coster and Goudsmit<sup>7</sup> have pointed out that the intensity results of Duane and Patterson are in fair agreement with the predicted values of Table I, except perhaps in the case of  $L\gamma_2$   $L\gamma_3$ .

TABLE II

*Results of Duane and Patterson on the relative intensities of L-series lines of tungsten.*

Lines	Relative intensities
$\alpha_1 : \alpha_2$	10 : 1
$\beta_1 : \beta_2 : \beta_3 : \beta_4$	100 : 55 : 16 : 9
$\gamma_1 : \gamma_2 : \gamma_3 : \gamma_4$	100 : 14 : 18 : 6

We have recently repeated the experiments of Duane and Patterson with improved apparatus. The x-ray tube with which we worked had a water-cooled copper anode containing a button of tungsten on which the cathode rays from a Coolidge cathode fell. The radiation used in the spectrometer left the tube through a mica window .002 cm thick. This tube was constructed of glass and was pumped continuously while in operation on account of unavoidable leakage around the mica window. The tube was run at 20 m-amp. and a constant voltage of about 30.7 kv obtained from a high capacity 50 kv storage battery. This battery and the general arrangement of the apparatus have been described elsewhere.<sup>10</sup> The beam incident upon the calcite crystal was limited by two slits 37 cm apart. After reflection from the crystal the beam entered the ionisation chamber through a mica window .002 cm thick. The ionisation chamber was filled with the vapor of methyl iodide. It was constructed of Pyrex glass after the design developed in this laboratory<sup>11</sup> except that, as in the experiments of Duane and Patterson, an open end with a ground flange was substituted for the usual blown glass window. On this flange a steel plate in which a slit had been cut was fastened with DeKhotinsky cement and the mica was then cemented on to the plate over the slit. The resulting ionisation chamber was air tight and gave satisfactory results.

<sup>10</sup> Armstrong and Stifler, J. Opt. Soc. Amer. and Rev. Sci. Inst. 11, 509 (1925).

<sup>11</sup> Blake and Duane, Phys. Rev. 10, 624 (1917); cf also for description, J. C. Hudson, J. Opt. Soc. Amer. and Rev. Sci. Inst. 9, 259 (1924).

The table which carried the crystal could be turned with precision through an angle of a few seconds and its position read by means of a traveling microscope sighted upon a Genevoise scale. The reflected beam was followed by turning the ionisation chamber through twice the angle traversed by the crystal after the well-known method of the Braggs.

The previous experiments of Duane and Patterson were made with the tube voltage slightly under 25 kv and with a tube which did not have a water-cooled target. By running our tube at 30,700 volts and 20 m-amp. we have been able to measure the relative intensities of the lines previously reported by Duane and Patterson with greater accuracy, and we have also been able to study some faint lines which they were not able to detect with certainty. The results which we have obtained agree well with the previous measurements.

#### THE $L\alpha$ LINES

Duane and Patterson give for the relative intensity of  $L\alpha_1/L\alpha_2$  the value 10. The predicted value (Table I) is 9.

We have made three measurements of the relative intensity of these lines. The resolution which we obtained was about the same as that shown in Fig. 3 of the previous report.<sup>3</sup> In this figure it is evident that the lines are not *completely* resolved, though doubtless they would appear so on a photographic negative. The base-line between  $\alpha_1$  and  $\alpha_2$  is not down to the level of the base-line on either side of the two lines. Elsewhere<sup>12</sup> we have described a method of estimating the relative intensities of such incompletely resolved lines based on the assumptions (1) that each line is single and of the same intrinsic wave-length breadth; (2) that the curve representing each line is symmetrical about the center of the line; (3) that the resolution is great enough so that the radiation due to a line is negligible at a wave-length  $\lambda \pm 2\Delta\lambda$  (where  $\Delta\lambda$  is the separation of the two lines). On the basis of these assumptions it is logical to take as a base-line for  $\alpha_1$  the total radiation intensity at an angle corresponding to the wave-length  $\lambda(\alpha_2) - \Delta\lambda$  and for  $\alpha_2$  the total radiation intensity at  $\lambda(\alpha_1) - \Delta\lambda$ . By assumption (1) the ordinate from the highest point on the line to the appropriate base-line for the line is proportional to its intensity. In this way we have been able to correct for incomplete resolution, though the correction is almost negligible in the case of  $L\alpha_2$   $L\alpha_1$ .

Our three measurements of the ratio of the intensities of  $L\alpha_1$  and  $L\alpha_2$  gave the results: 10.3, 10.7 and 9.1. The average is 10.0, the same value as that obtained by Duane and Patterson.

<sup>12</sup> Allison and Armstrong, preceding paper in this issue.

THE  $L\beta$  GROUP

Besides the strong lines  $\beta_1, \beta_2, \beta_3, \beta_4$  it is known from many researches<sup>13</sup> that a number of very faint lines lie in this region of the spectrum. In our present experiments we have been able to find evidence of  $\beta_5, \beta_6, \beta_7, \beta_9, \beta_{10}$ , though not of the line  $\beta_8$  nor of the lines  $\beta_{15}$  and  $\beta_{16}$  of Crofutt.<sup>13</sup> This result should not be interpreted as questioning the reality of the

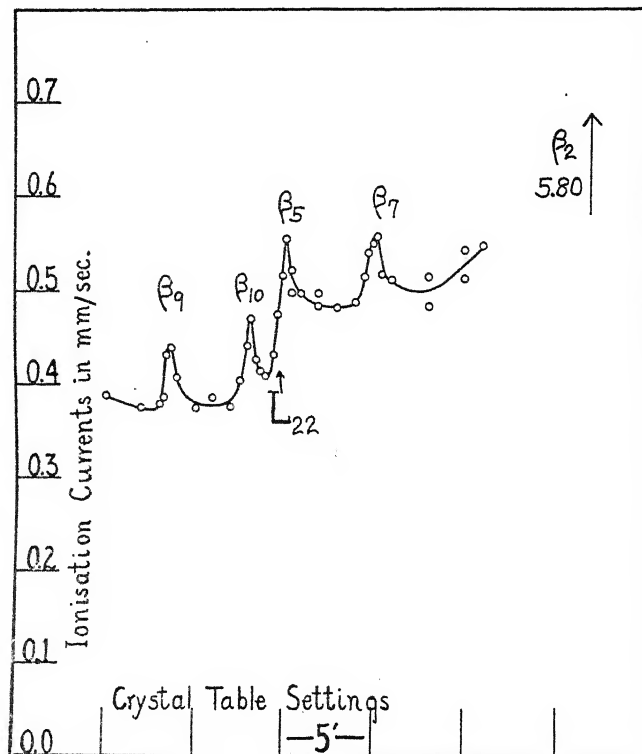


Fig. 1. Weak lines in the  $L\beta$  group.

lines, since they would undoubtedly appear with narrower slits than those we used. An attempt is now being made to separate  $\beta_2$  and  $\beta_{15}$  in the third order.

Some of the  $\beta$  lines are shown in Fig. 1. On account of the wide range in intensity of these lines it is not practical to plot all of them on the

- <sup>13</sup> E. Dershem, Phys. Rev. 11, 461 (1918);  
 O. B. Overn, Phys. Rev. 14, 137 (1919);  
 M. Siegbahn, Phil. Mag. 38, 639 (1919);  
 D. Coster, Phil. Mag. 44, 546 (1922), etc;  
 C. B. Crofutt, Phys. Rev. 24, 9 (1924).

same scale. The results of the measurements are given in Table III. The critical absorption of the target ( $L_{22}$ ) shows on the curve, and since  $\beta_9$  and  $\beta_{10}$  are on the short wave-length side, the values for these two lines given in Table III can be considered only as minimum ones. The

TABLE III

*Relative intensities of tungsten  $L\beta$  Lines.*

Date	$\beta_1$	$\beta_2$	$\beta_3$	$\beta_4$	$\beta_5$	$\beta_6$	$\beta_7$	$\beta_9$	$\beta_{10}$
May 19	(100)	51	16	8	....	2			
May 26	(100)	49	15	8	....	2			
June 13	(100)	48	14	7	....	2			
May 28	....	(49.3)	....	....	.5	....	....	.6	.3
May 29	....	(49.3)	....	....	.6	....	.6	.6	.6
June 11	....	(49.3)	....	....	.3	....	.2	.9	.9
June 11	....	(49.3)	....	....	....	....	....	.6	....
Averages	100	49.3*	15.0	7.7	0.47	2.0	0.4	0.68	0.60

\* This value includes the small satellite  $\beta_{15}$  found by Crofutt.

values for the very faint lines  $\beta_5$ ,  $\beta_7$ ,  $\beta_9$ ,  $\beta_{10}$  were difficult to reproduce in experiments carried out at different times. The slightest variation in the base-line due to general radiation and natural leak of the instrument was sufficient to change their apparent intensities greatly. The selection of a proper base-line for  $\beta_5$  is complicated by the presence of the  $L_{22}$  absorption on its short wave-length side. Consequently the relative intensities of these small lines among themselves are not highly reliable, though their order of magnitude with respect to the more intense lines is of interest. The lines  $\beta_9$  and  $\beta_{10}$  appear to be of about equal intensity.

The line  $\beta_6$ , which is not shown in the figure, appeared as a slight shelf on the long wave-length side of  $\beta_1$ .

Unfortunately, theoretical interpretations of most of the relative intensities which we have measured have not been advanced. The lines  $\beta_3$ ,  $\beta_4$ , however, have according to our measurements an intensity ratio which is not appreciably different from the value 2 predicted in Table I. The lines  $\beta_9$ ,  $\beta_{10}$  are generally supposed to represent transitions in violation of the selection principle, but at 30,700 volts, at least, they are of the same order of intensity as some of the permitted lines.

#### THE $L\gamma$ GROUP

In the  $\gamma$  group we have been able to obtain evidence of the lines  $\gamma_1$ ,  $\gamma_2$ ,  $\gamma_3$ ,  $\gamma_4$ ,  $\gamma_5$ ,  $\gamma_6$ . In some of the curves we obtained slight evidence of  $\gamma_8$ , but the height of the peak above the general radiation was very variable. At times there seemed to be indications of the lines  $\gamma_{11}$  and  $\gamma_{12}$  of Cro-

futt,<sup>13</sup> but these were very uncertain. These lines must be very feeble. Fig. 2 is a composite of some of the curves obtained in this region. We have included readings which showed the presence of  $\gamma_8$ , although this

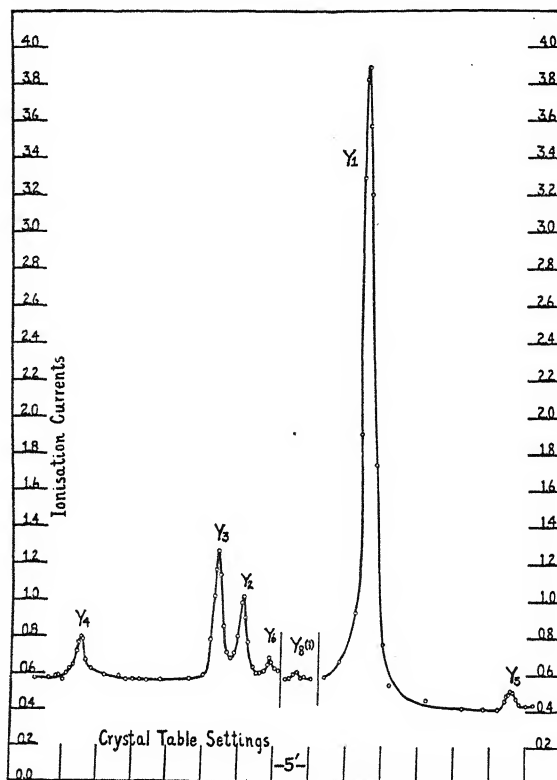


Fig. 2. The  $L\gamma$  group of the tungsten spectrum.

peak could not always be reproduced with the same intensity. The intensity results are shown in Table IV. The estimation of the intensity of  $\gamma_6$  is complicated by the absorption  $L_{21}$  which lies very near this line.

TABLE IV

*Relative intensities of tungsten  $L\gamma$  lines.*

Date	$\gamma_1$	$\gamma_2$	$\gamma_3$	$\gamma_4$	$\gamma_5$	$\gamma_6$	$\gamma_8$
May 21	(100)	14	24	....	....	3	1
May 22	(100)	14	22	....	3	1	1
May 25	(100)	14	21	7	....	3	
June 10	(100)	....	....	7	3	....	
Averages	(100)	14.0	22.3	7.0	3.0	2.3	1(?)

In the case of the lines  $\gamma_3$ ,  $\gamma_2$ , for which the intensity ratio predicted by Table I is 2, we find 1.59. Duane and Patterson found 1.29. If their curves are corrected for incomplete resolution by the method in use in this work, a value may be obtained more nearly like that given here. In this case, then, we may state with some confidence that there is at least an apparent exception to the extension of the rules of Burger and Dorgelo. The lines in question are close together, so that corrections due to absorption by materials in the path of the beam do not enter. The deviation from the rule is not in the direction to be corrected for by absorption effects outside of the ionisation chamber. The electron transfers which produce these lines pass through the M groups between their initial and final states in the N and L levels, and it is possible that this passage through intervening electron orbits may change the intensity ratio from the simple predicted value.

*Relative intensities of lines more widely separated in wave-length.*

It is of course of great interest to measure the relative intensity ratios for such pairs of lines as  $\alpha_1$ ,  $\beta_1$  and  $\beta_2$ ,  $\gamma_1$ , for which the predicted values are 9/5. The difficulties accompanying such determinations, however, have not as yet been surmounted. From the results of Unnewehr<sup>14</sup> it is possible to correct for the absorption in the mica windows of the x-ray tube and ionisation chamber. The experiments of Davis and Stempel<sup>15</sup> indicate that the percentage of the monochromatic incident beam reflected by the crystal does not vary rapidly enough with wave-length to introduce large corrections. The point of uncertainty occurs in the absorption of the x-rays by the target itself. This is indicated in our curves by the presence of the L critical absorptions, notably  $L_{22}$ . A very small effective absorbing layer of the target substance would be sufficient to alter greatly the relative intensity of two such lines as  $\alpha_1$  and  $\beta_1$ . In our experiments  $\beta_1$  was slightly more intense than  $\alpha_1$ , while  $\gamma_1$  was somewhat more than half as intense as  $\beta_2$ . It seems inadvisable to attempt to give values for use in testing theoretical predictions. Yet since the correction for absorption would change both ratios in the same direction, it could not bring them both to the value 9/5.

An interesting interpretation of the relative intensities in the  $K\alpha$  doublet has been given by Stoner,<sup>16</sup> who points out that the observed ratio 2 may be taken as an indication that there are twice as many electrons in the  $L_{22}$  orbit as in the  $L_{21}$  orbit. He has extended this idea

<sup>14</sup> E. C. Unnewehr, Phys. Rev. **22**, 529 (1923).

<sup>15</sup> Davis and Stempel, Phys. Rev. **17**, 608 (1921).

<sup>16</sup> E. C. Stoner, Phil. Mag. **48**, 719 (1924).

to such lines as  $L\beta_3$ ,  $L\beta_4$ , in which the influence of intervening electron levels is presumably small. Thus the observed intensity ratio 2 for  $L\beta_3$ ,  $L\beta_4$  is taken to be evidence that there are twice as many electrons in the  $M_{22}$  orbit as in the  $M_{21}$ . If the perturbing effect of the L levels on the  $K\beta$  transitions from M to K is small, our result of 2 for  $K\beta_1/K\beta_3$  could be used as additional evidence of the relative numbers of electrons in  $M_{22}$  and  $M_{21}$ . In the case of  $L\gamma_3/L\gamma_2$ , as Stoner has anticipated, there is a deviation which may well be due to the influence of intervening levels. Sommerfeld<sup>6</sup> has pointed out that the relative intensities of the

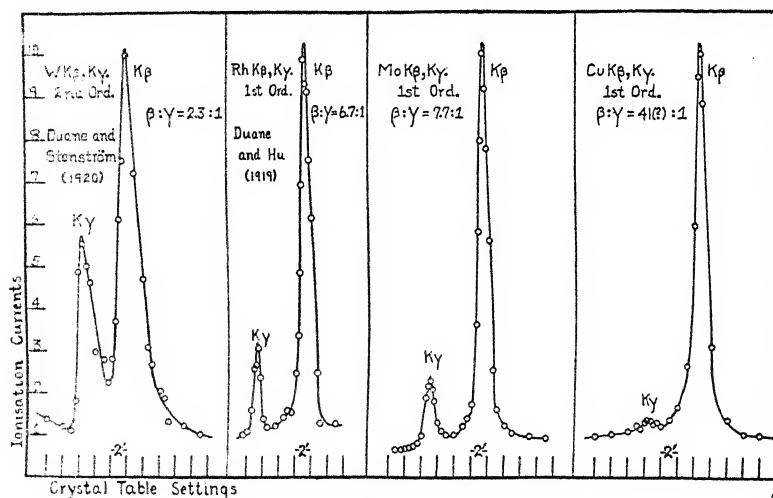


Fig. 3. Relative intensity of  $K\beta$  to  $K\gamma$  for W, Rh, Mo and Cu.

components of compound doublets are probably not related to the numbers of electrons in the orbits in the simple manner considered by Stoner.

#### INTENSITIES IN THE COPPER K SPECTRUM

The copper K spectrum was emitted strongly from the copper part of the anode. Siegbahn and Žáček<sup>8</sup> have measured the relative intensities of  $\alpha_1 : \alpha_2 : \beta_1$  in the copper K spectrum and find 100 : 51.2 : 25.

We have made two measurements of the intensity ratio of  $\beta/\gamma$ . The  $\gamma$  line is extremely weak, and on account of the presence of the critical absorption in its immediate vicinity, estimates of its intensity are quite uncertain. For these two lines we have taken the difference between the highest point on the curve and the base-line as proportional to the intensity, since the uncertainty with regard to the  $\gamma$  line makes the more



accurate method of area comparison superfluous. We obtained the values 100/2.7 and 100/2.2 for the intensity of  $\beta$  relative to  $\gamma$ .

It is known that the  $\gamma$  line becomes relatively weaker with decreasing atomic number, and we have drawn Fig. 3 to illustrate this fact. The values for tungsten are taken from the results of Duane and Stenström.<sup>2</sup> The curve for rhodium is obtained from one shown by Duane and Hu.<sup>4</sup> The numerical value of the intensity of Rh  $K\beta$  relative to  $K\gamma$  was determined by us by the method of areas. The curve for molybdenum is from the preceding paper.<sup>12</sup>

We have also examined the spectrum in the region of the non-diagram copper lines  $Ka_3$ ,  $Ka_4$ , reported by Dolejsek and by Dolejsek and Siegbahn.<sup>17</sup> These lines have been interpreted as spark lines by Wentzel.<sup>18</sup> At 30,700 volts we could find no good evidence of this doublet, although the Cu  $Ka_2$ ,  $Ka_1$  lines were very strong. The relative intensity of  $Ka_3$ ,  $a_4$  to  $Ka_1$  at this voltage must be less than 1/100. It is well known that in elements lighter than copper the intensity of these "spark" lines is greater relative to the lines due to the singly ionised atom.

We are greatly indebted to Professor William Duane for his valuable suggestions and kindly criticisms.

CRUFT HIGH TENSION ELECTRICAL LABORATORY,  
HARVARD UNIVERSITY,  
August 11, 1925

<sup>17</sup> Siegbahn, *Spektroskopie der Röntgenstrahlen*, p. 102.

<sup>18</sup> G. Wentzel, *Ann. der Physik* **66**, 437 (1921).

THE APPARENT SHAPE OF X-RAY LINES AND ABSORPTION LIMITS<sup>1</sup>BY F. K. RICHTMYER<sup>2</sup>

## ABSTRACT

Effect of instrumental factors on the observed intensity distribution of x-ray lines and at absorption limits.—(1) *Slit width*. In the case of two slits of equal width, sharp lines reflected from a perfect crystal should give an isosceles triangle distribution. If the two slit widths are unequal, the triangle is truncated; this may shift the relative position of the lines of a partly resolved doublet. (2) *Slit height* widens the isosceles triangles slightly, making the long-wave-length side less steep. (3) *Non-uniform energy distribution over the focal spot* produces corresponding lack of symmetry. An actual distribution curve obtained with very narrow slits showed two unequal maxima near the edges of the spot. The same three factors affect the apparent sharpness of the absorption limit. In particular, the finite slit width results in the rounding off of a sharp discontinuity into a skew-symmetrical S curve consisting of parts of two parabolas whose axes are vertical and separated a distance equal to the angular slit width.

**Intensity distribution in the  $K_{\alpha}$  doublet of Mo.**—The curves correspond to monochromatic lines of width .0003A or less. The relative intensity is very close to 2 (2.01). There is no line between them with intensity greater than 1 percent that of  $K_{\alpha 1}$ .

**Sharpness of the K absorption limit of Ag.**—The curve obtained agrees with that for a limit which is sharp within experimental error, .0002A.

THE x-ray spectrometer used by the writer in studying absorption coefficients needs frequent calibration. For this purpose the several orders of the K series of the target-element (usually tungsten or molybdenum) have been used. In this connection certain peculiarities and characteristics of the x-ray spectrometer have been observed, which seem not without interest and which should be given consideration in studying the actual shape of x-ray lines and absorption edges and in making precision wave-length measurements.

The spectrometer is of the usual Bragg type. The x-ray beam is limited by two slits 38 cm apart placed between crystal and target. Each slit is about 2 cm high and is formed by two lead jaws 1 cm wide, ground plane, and very carefully adjusted to parallelism. The jaws may be moved

<sup>1</sup> This paper is based in part on papers read in February and April, 1924, before meetings of the American Physical Society. (See Richtmyer and Spencer, *Phys. Rev.* 23, pp. 550 and 760.) The author takes pleasure in expressing his appreciation of the assistance rendered by Mr. Spencer.

<sup>2</sup> This work has been made possible by a grant to the author from the Heckscher Research Council of Cornell University.

bi-laterally by micrometer screws reading to .0001 inch (.0025 mm). The tube is adjusted so that the plane of the target makes an angle of about  $8^\circ$  with the line of the slits, the focal spot thus being equivalent to an ellipse approximately 15 mm high and 2 mm wide. The crystal is of calcite, a very perfect one kindly loaned to the writer by Professor Bergen Davis. Ionization currents are read in the usual way, by means of an electrometer of the Compton type.

#### FACTORS AFFECTING THE APPARENT SHAPE AND WIDTH OF LINES

Fig. 1 represents a typical calibration curve showing the first-order lines of Mo and taken with slits .075 mm wide.<sup>3</sup> The abscissas represent

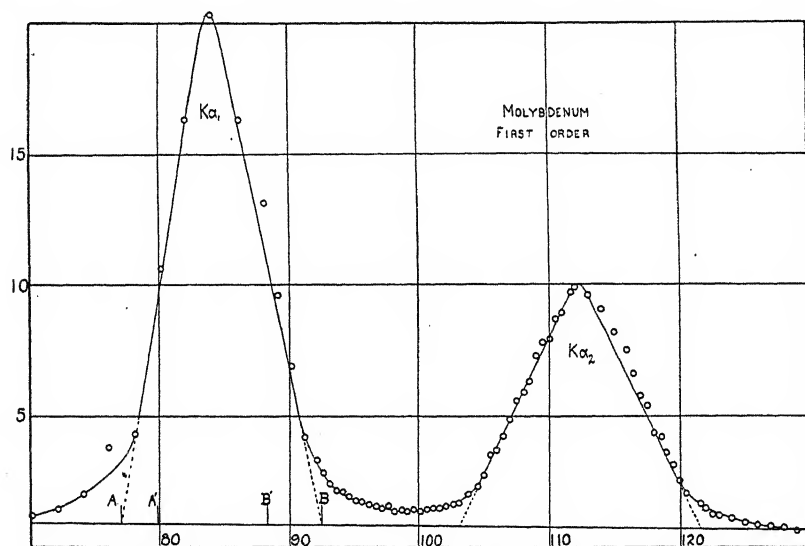


Fig. 1. The first order  $K\alpha$  lines of Mo as used in calibrating the spectrometer. The lines are approximately triangles, but are slightly convex outward on the right (long wave-length) side.

arbitrary divisions on the scale of the spectrometer, each division corresponding approximately to .00015Å. It will be noted that each line is approximately a triangle *but with the long wave-length side slightly convex outward*. It was this observation which started this investigation of the *instrumental factors* affecting the apparent shape of x-ray lines. Omitting the effect of the crystal<sup>4</sup> these factors are:

<sup>3</sup> This curve was taken with some care in order to investigate the region between  $K\alpha_1$  and  $K\alpha_2$  where it had been suggested to the author that a faint line might be found. It is quite obvious that no such line of appreciable intensity exists.

<sup>4</sup> See Bergen Davis and W. M. Stempel, Phys. Rev. 19, p. 504 (1922).

- (1) The width (actual and relative) of the slits limiting the beam.
- (2) The "brightness" of different parts of the focal spot.
- (3) The height of the slit.

*The effect of slit width.* In what follows we shall assume that we are dealing with a strictly monochromatic line of wave-length  $\lambda$ , and with a perfect crystal which reflects  $\lambda$  at the angle  $\theta_\lambda$  given by the usual equation

$$n\lambda = 2d \sin \theta_\lambda$$

In Fig. 2A let the two limiting slits be a distance  $D$  apart and have the same width  $s_1$ . (In any actual case  $D$  is very large compared to  $s_1$ .) Let  $TT$  be the focal spot, the major axis of the ellipse being at right angles to the paper. The crystal, not shown, is at the right of the figure and is capable of rotation about an axis perpendicular to the plane of the

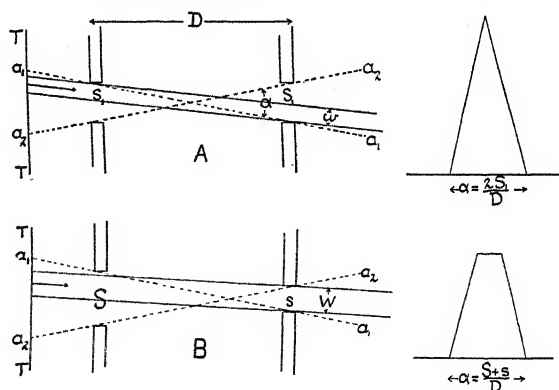


Fig. 2. Showing diagrammatically the effect of finite slit widths on the apparent shape of a line.

figure. Let the angular position of the crystal be measured, in the usual way, by the angle  $\theta$  which the crystal planes make with the line passing through the centers of the two slits.

Starting from  $\theta = 0$  and turning the crystal counter-clockwise, no reflection of the line  $\lambda$  will be observed until the crystal planes make an angle  $\theta_\lambda$  with the line  $a_1a_1$  which is defined by the far edge of the left-hand slit and the near edge of the right-hand slit. As the crystal is rotated beyond this position the planes make the angle  $\theta_\lambda$  with a beam of parallel rays of width  $w$ , as shown in the figure. This width  $w$  will increase and the *apparent* intensity of the reflected line will accordingly increase until the crystal position is such that  $w$  is equal to the slit width  $s_1$ . Beyond this point  $w$  will decrease to zero when the crystal makes the angle  $\theta_\lambda$  with the line  $a_2a_2$ . Since  $s_1$  is always very small compared to  $D$  this change of  $w$  (increase or decrease) is a linear function of the angular position of the crystal. Hence the *observed* shape of the line

should be a triangle with a base of which the *angular* width is given by  $2s_1/D$ .

If the slits be of *unequal* width, say  $S$  and  $s$  as in Fig. 2B, similar considerations show that the apparent shape of the line will be an isosceles trapezoid of which the base has the angular width  $(S+s)/D$ .

Parenthetically, it is interesting to point out that the apparent shape of a close doublet will be materially influenced accordingly as the measurements are made with equal or unequal slits. Fig. 3A shows, diagrammatically, the apparent shape of a doublet, such as  $K\alpha_1, \alpha_2$ , when observed by slits of unequal width. The inevitable rounding off of the corners would make this appear as a single line with the maximum at  $h$  instead of  $h_1$ . Fig. 3B shows the appearance of the doublet when slits of equal width are used. The maximum of the more intense line appears in its correct position, and the presence of the weaker component is indicated by irregularity on the side of the curve.

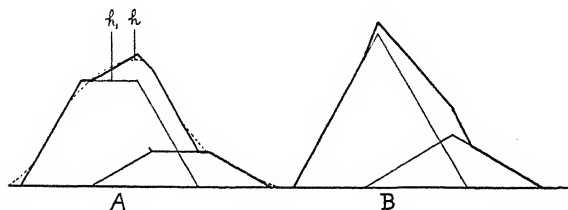


Fig. 3. A. The apparent shape of a doublet when observed by slits of unequal width. B. Same for slits of equal width. Curve A would evidently lead to an incorrect location of the more intense line.

*The effect of variation of "brightness" in the focal spot.* Referring to Fig. 2A it is readily observed that the apparent shape of the line can be a perfect isosceles triangle only if there is a constant x-ray brightness over that part of the focal spot falling within the solid angle defined by the slits (the angle between the lines  $a_1a_1$  and  $a_2a_2$ ). There is reason to expect such variation of brightness, partly because of space charge effects within the electron stream from filament to target, partly because of the dissymmetry in field introduced in tubes where the target makes an angle of  $45^\circ$  with the axis of the tube.

To test this point, the slits  $s$  were made very narrow (less than .025 mm), thereby isolating a very narrow vertical strip ( $aa$  Fig. 4) of the focal spot, parallel to its major axis. Using the direct beam, the intensity of the radiation was measured as the tube was moved by micrometer adjustment, so as to cause the focal spot to move past the axis of the slits. The resulting curve is shown in Fig. 4. The distance  $R$  on the graph corresponds to the minor axis of the focal spot as seen from the slit

system. Two maxima, *A* and *B*, are observed indicating that there is a ring of greater intensity just inside the focal spot, but that the one edge of the ring, *B*, is more intense than the other.

From Fig. 2A it is obvious that dissymmetry will be introduced into the triangle if for example the adjustment of the focal spot should be such that the hump *B* corresponds to point  $a_1$  and some point midway between the two humps corresponds to  $a_2$ . Something like this was apparently the case when the data for Fig. 1 were taken.

To test these two points the slits *s* were carefully adjusted to .038 mm each, and the tube was so placed that the flat part of the curve, between *A* and *B* of Fig. 4, coincided with the region  $a_1a_2$  of the focal spot in Fig.

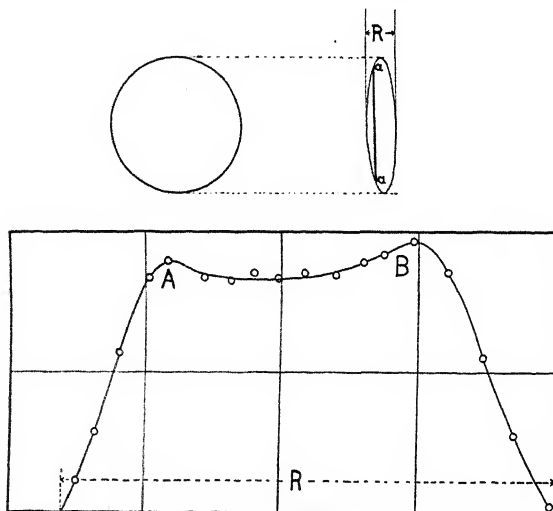


Fig. 4. The unequal distribution of energy across the focal spot of a tube. The focal spot is seen from the spectrometer as an ellipse with minor axis *R*.

2A. A run was then taken on the line  $Ka_1$ . The result is shown in Fig. 5. It is observed that the sides of this line correspond to the sides of a triangle, and that there is lateral symmetry, instead of the convexity observed in Fig. 1. The width of the base of the triangle is somewhat greater than predicted from the known slit width. But it is rather difficult to measure with high precision slit widths as narrow as .038 mm.

In the case of Fig. 1, the graph shows data taken with slits .076 mm wide. The full line just above the abscissa scale, represents, as nearly as could be estimated, the white radiation in the same region. Therefore one may find the width of the base of the triangle, for  $a_1$  for example, by projecting the sides down to this base line. In this way it is found that with these slits, the width of the base *AB* corresponds to an equivalent

wave-length range of .00232A. The slits were then narrowed to .038 mm and another run taken. The data are not plotted but the base line was observed to be  $A'B'$ , corresponding to an equivalent wave-length range of .00136A. Extrapolating from these two results, zero slit width would correspond to a wave-length range of .0003A. That is to say, so far as these observations go the line  $K\alpha_1$ , is monochromatic to this extent. However, because of the difficulty of making precise measures of slit widths as small as these, not too much dependence should be put on this result.

Another point of some little importance when one is concerned with measuring wave-lengths to the highest precision, is brought out by the

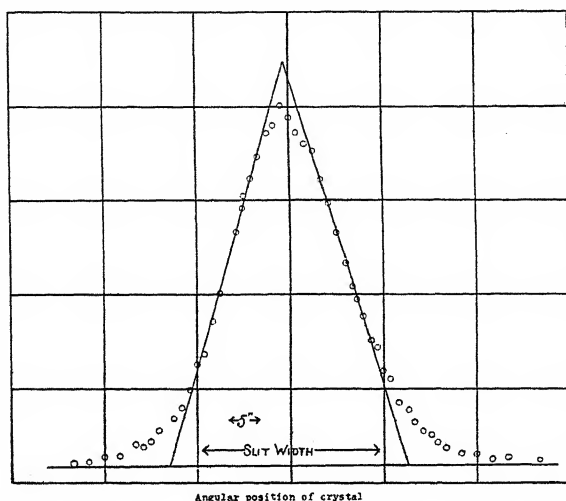


Fig. 5. The  $K\alpha_1$  line of Mo (first order), taken with slits of equal width and with the tube so adjusted as to give nearly equal energy distribution over the part of the focal spot used.

$K\alpha_2$  line of Fig. 1. As has been pointed out above, the long wave-length side of the graph is convex outward because of the irregular distribution of energy over the focal spot. Had a smooth graph been drawn through these points and the *maximum* taken as the exact location of the line this maximum would differ from the one shown in the graph by approximately .00015A. While this difference is not large, it shows that the position of a line may be misjudged by an appreciable amount unless care be taken to work with equal energy distribution on the target.

*The effect of slit height.*<sup>5</sup> For most purposes this effect can be neglected but in work aiming at high precision it is of sufficient importance to be

<sup>5</sup> See also article by H. S. Uhler, Phys. Rev. 11, p. 11 (1918).



worthy of mention. To simplify discussion, assume that the axis of rotation of the crystal is vertical and that the crystal planes are parallel to this axis; also that the slits limiting the x-ray beam are, as above, between crystal and tube (and are, of course, vertical). It is then usually assumed that the angle  $\theta$  in the equation

$$n\lambda = 2d \sin \theta$$

is measured by the angle between the *plane* of the crystal face and a second plane passing through the axis of rotation and the two slits. This is obviously the case only for those rays which are *horizontal*. On account of the finite height of the slits there will be other rays, not horizontal, passing through the slit system. For a ray which makes an angle  $\varphi$  with the horizontal, the glancing angle  $\theta$  at which it meets the crystal planes, is given by the equation

$$\sin \theta' = \sin \theta \cos \varphi.$$

If the wave-length of this ray be  $\lambda$ , then the angle  $\theta_\lambda$  at which it will be reflected will be given by

$$\sin \theta_\lambda = \sin \theta' = \sin \theta \cos \varphi,$$

or

$$\sin \theta = \sin \theta_\lambda / \cos \varphi;$$

that is, the greater the divergence of the ray from the horizontal the greater must be the angle  $\theta$  for reflection to take place. In any actual case  $\varphi$  is small, and its maximum value is given very nearly by the angle which the slit nearest the ionization chamber (or photographic plate) subtends at the slit farthest away from the chamber. The net result of this effect, with very narrow slits and a crystal thin enough to eliminate the penetration error, is to produce a reflected beam, as the crystal is turned, of which the cross section is similar to the cross section of a plano-concave lens, the plane side being sharp and turned toward shorter wave-lengths, while the curved side is slightly diffuse. For this reason the long wave-length side of the triangles, such as in Fig. 1, should be not quite so steep as the short wave-length side. *This effect is observed in practically every case.* To illustrate the magnitude of the effect, it may be pointed out that for a value of  $\varphi$  of  $1^\circ$ , the observed position of the  $K\alpha$  lines of Mo will be shifted about  $4''$  from the true position, in the first order.

*Monochromaticity.* A question closely allied to the above is the extent to which the degree of monochromaticity of a reflected beam of white radiation is influenced by the finite width and height of slits. From the law of the crystal grating it follows by differentiation that

$$d\lambda = (2d/n) \cos \theta \, d\theta$$

from which, by knowing the angular divergence  $d\theta$  of the reflected beam the value of  $d\lambda$  can be obtained. From what has been said above it is obvious that  $d\theta$  is made up of two parts, a part  $\alpha$  due to the finite width of the slits and a part  $\delta$  due to finite height of the slits. By reference to Fig. 2 it is readily seen that  $\alpha$  is equal to twice the angle subtended by the width of one of the limiting slits at the other, if the slits be of equal width. We can compute  $\delta$  as follows. From the preceding section

$$\sin \theta' = \sin \theta \cos \varphi_m$$

where  $\varphi_m$  now represents the *maximum* value of  $\varphi$  and is approximately the vertical angle subtended by the slit nearest the chamber at the slit

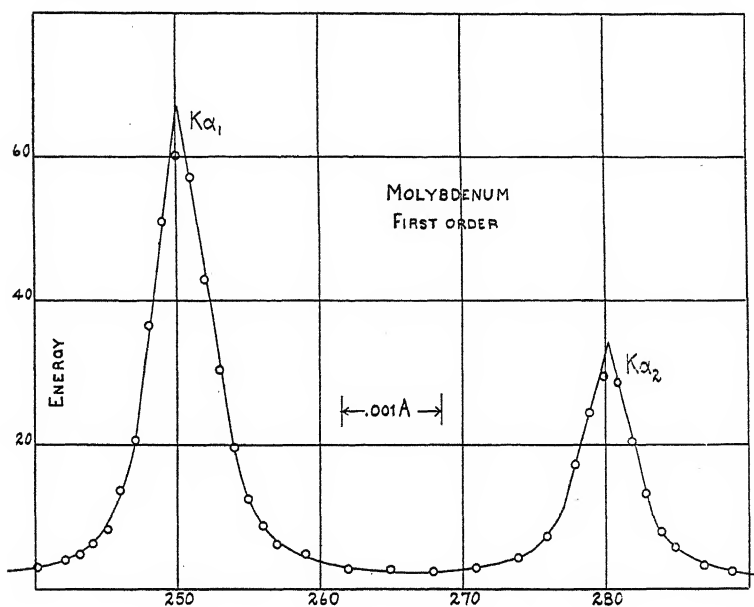


Fig. 6. The  $K\alpha$  lines of Mo (first order), taken with slits .0025 cm wide and 38 cm apart, showing that the curve for each line is an almost symmetrical triangle. Measured from the white radiation in the neighborhood, the height of  $\alpha_1$  is almost exactly twice that of  $\alpha_2$  (65.0/32.3). Note also the high resolving power.

farthest away, assuming the slits to be of equal height. Then

$$\delta = \theta - \theta'$$

Fig. 6 gives observations of the  $K\alpha$  lines of Mo in the first order taken with the spectrometer described above using a calcite prism. The slits were all approximately 2.5 cm high. The slits limiting the beam were .025 mm wide and 38 cm apart. This gives a value of  $\alpha$  of .00013 radian. The distance between the slits nearest and farthest from the ionization

chamber was about 100 cm, from which it is computed that  $\delta$  is .000025 radian. Hence

$$d\theta = \alpha + \delta = .000155 \text{ radian}$$

and

$$d\lambda = .00094\text{\AA}$$

or about one fifth of the distance between the  $K\alpha$  lines. This agrees with the excellent resolution shown in Fig. 6. In spite of this high resolution the radiation between the two lines is slightly greater than is to be expected from the magnitude of the white radiation on either side of the doublet. This may possibly be due to slight crystal imperfections. The effect is much more apparent in Fig. 1.

#### THE APPARENT WIDTH OF THE ABSORPTION LIMIT

The methods used in determining the effect of the slit system on the apparent shape of x-ray lines may be applied equally well to absorption limits. Assume, as before, that we are dealing with a perfect crystal and further that the absorption limit of the absorber used is infinitely sharp and occurs at wave-length  $\lambda_K$ . We will also assume that the target has no characteristic lines in this neighborhood, so that we are dealing only with the white radiation. Let  $I$  be the intensity of this white radiation, practically constant over the very narrow spectral region concerned. Let  $\beta_1$  and  $\beta_2$  be the fractional transmission coefficients on the short wave-length side and long wave-length side, respectively, of this absorption limit, and let the corresponding intensities be  $\beta_1 I$  and  $\beta_2 I$ . Then on account of the finite slit widths the apparent absorption break will not be sharp, if high resolving power be used, but the rise from  $\beta_1 I$  to  $\beta_2 I$  will be gradual.

We can regard the continuous spectrum coming through the absorber as made up of a large number of adjacent lines, the intensity of which (see Fig. 7C) suddenly rises from  $\beta_1 I$  to  $\beta_2 I$  as the absorption limit is passed. These in turn can be regarded as a series of lines of intensity  $(\beta_2 - \beta_1)I$  superimposed on the spectrum  $\beta_1 I$ . When the crystal is set at such an angle that none of the "lines"  $(\beta_2 - \beta_1)I$  are reflected, the observed intensity will be constant and equal to  $\beta_1 I$ ; but when the slit approaches the absorption limit<sup>6</sup> some of the "lines," will be reflected, each line giving rise to a triangle, as previously discussed, the base of the triangle being determined by the slit widths. The actual observed intensity, at any crystal angle, will be the sum of the intensities due to each of the separate triangles (Fig. 7B), i.e. the sum of the intercepts which the sides of the several triangles make on an ordinate erected at the abscissa corresponding to the crystal setting. Thus Fig. 7C repre-

<sup>6</sup> The "lines" are assumed narrow compared to the slit system.

sents the "lines" forming the transmitted spectrum, the absorption break occurring at  $\theta_k$ . To each line 1, 2, 3, . . . there corresponds a triangle 1, 2, 3, . . . (Fig. 7B) the base of which is defined by the slit width. If the crystal be set at the angle  $\theta_k$ , the energy observed at that setting will be proportional to the sum of the intercepts made on that ordinate by the first four triangles. This corresponds to point  $p$  of Fig. 7A. The locus of point  $p$ , from  $b$  to  $o$  is a parabola, tangent at  $b$  to the line  $ab$  and meeting, tangentially at  $o$  another similar parabola which is the locus of  $p$  from  $o$  to  $c$ , the latter parabola being tangent to the line

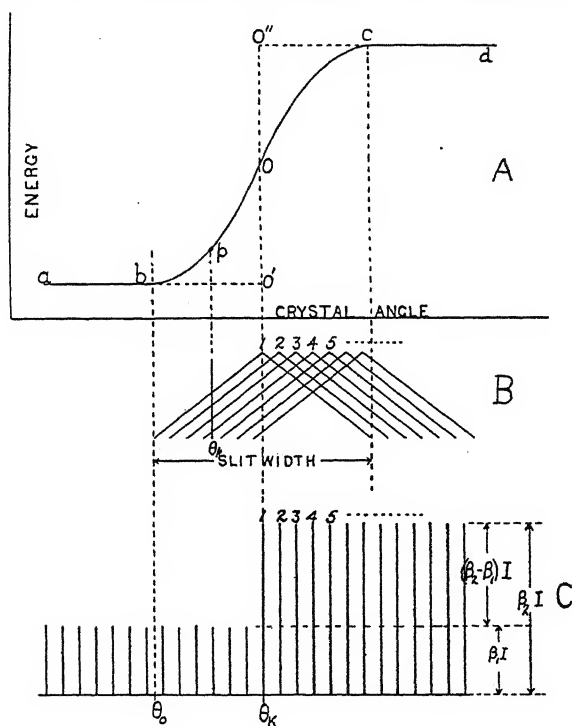


Fig. 7. Showing diagrammatically how the finite slit width determines the apparent shape of an absorption break.

$cd$  at  $c$ . The line  $ab$  represents the constant intensity  $\beta_1 I$ , and the line  $cd$  the constant intensity  $\beta_2 I$ . For infinitely narrow slits the absorption break would be given by the line  $o'o''$ . For slits of finite width the absorption break is given by the line  $boc$ , the angular distance  $bc$  being exactly equal to the angle of the slits.

Fig. 8 shows such an energy distribution curve taken through the K limit of silver. The points  $abocd$  correspond to similar points in Fig. 7A. The full line  $boc$  is a *theoretical* curve, made up of two parabolas

tangent at  $a$  and  $c$  to the lines  $ab$  and  $cd$  respectively, and meeting each other tangentially at point  $o$ . The circles are actual observations. The observed points are seen to agree exceptionally well with the theoretical curve between  $b$  and  $c$ .

Furthermore it is to be noted that the actual observed width of the discontinuity agrees *within the limit of error* with the slit width, the difference being certainly not more than 4 percent. That is to say, the

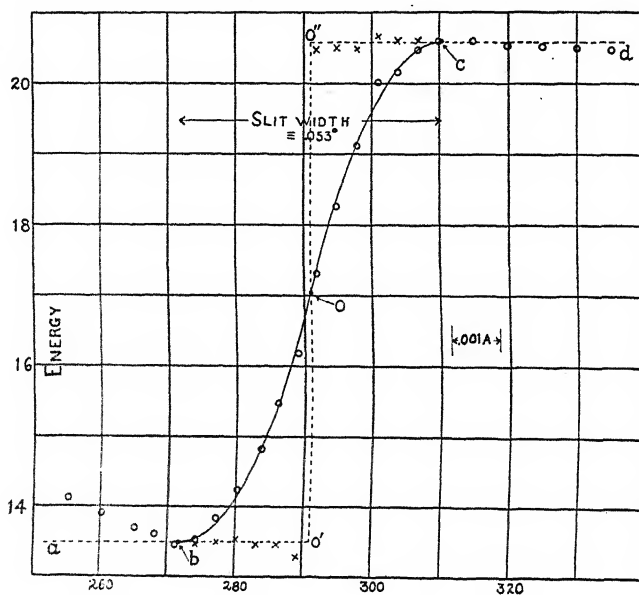


Fig. 8. The K absorption limit of silver, determined by taking an energy distribution curve of the white radiation from a Mo target with a silver absorber in the path of the beam. The curve  $abcd$  is a theoretical curve based on the known slit widths used. The circles are observed points. The crosses are the result of correcting the readings for slit width error. Note the sharpness of the absorption break.

K discontinuity of silver is sharp to this extent, the real width of the discontinuity, if it is different from zero, being probably less than  $.0002\text{\AA}$ .

It is now a very simple matter to plot a corrected discontinuity curve, eliminating the effect due to slit width. It is only necessary to move each observed point between  $b$  and  $o$  *downward* by the distance between the theoretical curve and the straight line  $ab$ , extended at that point. Similarly, each point between  $o$  and  $c$  should be moved upward. This has been done; the resulting points are represented by crosses. As noted in the preceding paragraph, the discontinuity is sharp within the limits of error of this experiment.

By this method it is possible to get values of the mass absorption coefficient very close to the absorption limit.

The author takes pleasure in expressing his very great obligations to the Research Laboratory of the General Electric Company for making available certain very essential parts of the equipment used in this investigation.

CORNELL UNIVERSITY,  
July 2, 1925.

## THE LATTICE PARAMETER AND DENSITY OF PURE TUNGSTEN

BY WHEELER P. DAVEY

## ABSTRACT

Because of the importance of knowing the values of these constants as accurately as possible, x-ray diffraction patterns were made for several samples differently treated as follows, (1) W plus 10 parts flour in comparison with NaCl in the other end of specimen tube; (2) the same in comparison with Au plus 10 parts flour, and (3) W plus 10 parts NaCl. The results agree within the reproducibility of the results, .001 to .003A, with the values previously obtained for *lattice parameter* ( $a = 3.155 \pm .001$ ) and *density* ( $D = 19.32 \pm .02$ ).

THE most accurate determinations of the diameters of fine wires are made in terms of their length and weight. All calculations of efficiency of light emission and of thermionic emission of W wires depend therefore upon a knowledge of their density. Experiment shows<sup>1</sup> that, within the experimental error, these W wires have the same lattice parameter as pure annealed W powder, so that the density of both must be identical. It therefore seemed desirable to attempt to check the value of the lattice parameter of pure W (99.999 percent) which was published recently.<sup>1</sup> That value was obtained in terms of the lattice parameter of NaCl. The W powder, diluted with ten times its volume of wheat flour so as to reduce its opacity to the x-rays, was inserted in one end of a specimen tube. NaCl diluted with its own volume of flour was in the other end. In this way the two diffraction patterns were obtained side by side on the same photographic film.

There was a possibility that the W had not been sufficiently diluted, so that the equivalent centers of the W and NaCl might not have been in the same straight line. This would have made the lattice parameter of W come out too small, thus giving too high a value for the density. A portion of the same lot of W was therefore mixed directly with ten times its volume of NaCl, so that the two diffraction patterns were superimposed.<sup>2</sup> In this way the equivalent centers of the W and of the NaCl were necessarily identical. Measurements of the lattice parameter of W made in this way were therefore free from any possible objection which might have been raised against the previous measurement. Pure Au furnishes a second check. The parameter of 99.999 percent Au previously

<sup>1</sup> Davey, Phys. Rev. 25, 753 (1925).

<sup>2</sup> Havighurst, Mack and Blake, J. Amer. Chem. Soc. 46, 2368 (1924).



published<sup>1</sup> gives a density which agrees within the error of experiment with the highest density found for Au by the ordinary methods.<sup>3</sup> Since the admixture of any impurities in gold must necessarily lower the density, this was taken to mean that the published parameter for pure Au was correct. A portion of the same sample of Au was mixed with ten times its volume of flour and inserted in one end of a specimen tube as a calibration standard. A portion of the original lot of W was mixed with ten times its volume of flour and inserted in the other end. The two diffraction patterns were thus obtained side by side. The two metals were both of such high atomic number that any error caused by differences in the equivalent centers of the two must have been negligible.

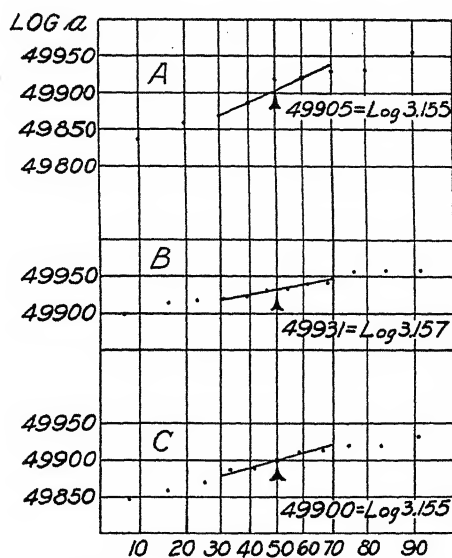


FIG. 1. Probability curves for the lattice parameter of tungsten.

- A. W plus 10 parts flour; NaCl plus 1 flour at other end of specimen tube.
- B. W plus 10 NaCl; calibration in terms of NaCl.
- C. W plus 10 flour; Au plus 10 flour at other end of specimen tube.

Every line in the W diffraction pattern corresponding to an interplanar distance of less than 2.00Å was corrected in terms of the calibration pattern on the same film, and each of these corrected readings was made to give a value of the lattice parameter. These results were then plotted on probability paper as previously described<sup>4</sup> to find the most probable values of the parameter. The reproducibility of such a result is  $\pm 0.1$  percent for ordinary diffraction patterns. For the data originally pub-

<sup>3</sup> Averkieff, *Zeits. anorg. Chem.* 35, 329 (1903).

<sup>4</sup> Davey, *Phys. Rev.* 19, 538 (1922).

lished the lines were so fine that the reproducibility was considered to be  $\pm 0.03$  percent. The probability curves for films from all three methods are given in Fig. I. It is interesting to note that, in every case, if the curve is lifted or lowered to the level of the point which lies furthest off the curve, the value of the lattice parameter  $a$  is not changed by more than  $0.001A$ .

The three methods give for the value of the lattice parameter of W,  $3.155 \pm .001A$ ,  $3.157 \pm .003A$ , and  $3.155 \pm .003A$ , where  $\pm$  refers to the degree of reproducibility of the data. It therefore seems justifiable to retain the original value  $3.155A$ . The close agreement between the results given by the two methods of using the NaCl for calibration is at first sight surprising. It must mean that when W is mixed with as much as ten times its volume of flour, the dilution is sufficient to provide direct paths through the specimen through which the x-ray beams may travel to and from each particle of W with little or no absorption. Such a result was hardly to have been expected.

This parameter gives a density of  $19.32 \pm .02$ . As was pointed out in the original paper this is much higher than the values published in Van Nostrand's Chemical Annual and in Groth's Chemische Krystallographie. It is, however, consistent with the value 19.3 published by Fink<sup>5</sup> for rods 3.75 mm in diameter.

RESEARCH LABORATORY,  
GENERAL ELECTRIC COMPANY,  
SCHENECTADY, N. Y.  
AUGUST 17, 1925.

<sup>5</sup> Fink, Trans. Amer. Electrochem. Soc. 17, 229 (1910).

## SOFT X-RAYS FROM IRON, COBALT, NICKEL AND COPPER

BY CHARLES H. THOMAS

## ABSTRACT

Critical potentials of Fe, Co, Ni and Cu, to 1500 v.—Using the photo-electric method previously described,<sup>1</sup> the study of iron has been extended, and critical potentials of Co and Ni have been determined throughout the range 0-1500 volts. The arrangement is more sensitive than that used by previous observers and readings were taken at intervals of 1/2 volt accelerating potential up to 100 volts and at corresponding small intervals for the higher ranges; hence the curves are more accurate and reproducible than those obtained by other investigators. Forty-six critical potentials were found for Ni, 48 for Co, and the number for Fe was increased to 46. More than 100 independent curves were obtained for each of these metals and the breaks reported were entirely reproducible. Copper was investigated only in the range 0-90 and 700-1200 volts; 25 critical potentials were found. The breaks are of two types with shapes which suggest that they correspond to ionizing and radiating potentials. There is a general correspondence, both in nature and value, between the critical potentials of iron, cobalt and nickel, with an upward shift of voltage with increasing atomic number. This correspondence is especially striking in the case of the nine breaks which have been designated as "ionizing" potentials. In the region of the L series, the critical potentials of copper also correspond accurately with those of the other metals, but in the region 0-90 volts there appears to be no similarity. The critical potentials which could be connected with *x-ray spectroscopic terms* with some certainty are: Fe,  $L_I$  at 818.5 and  $L_{III}$  at 704.3; Co,  $L_I$  at 873.2 and  $L_{III}$  at 764.8; Ni,  $L_I$  at 948.0 and  $L_{III}$  at 833.4; Cu,  $L_I$  at 1017.0 and  $L_{III}$  at 929.0 volts.

IN a previous paper<sup>1</sup> the writer has described a method and apparatus for the accurate determination of critical radiating potentials. This apparatus, based on a photo-electric detection of x-radiation, differs from previous apparatus of the same sort in that the detecting electrode completely surrounds the target, so as to intercept all the radiation emitted from it. The method is distinguished by extraordinary precautions to secure steadiness, especially in the thermionic emission from the Coolidge cathode, and in the use of small voltage intervals in covering the desired range of voltages. Details of the apparatus and operation are given in the preceding paper.

In the present paper a further study of iron is described, since spring weather conditions interfered with some of the earlier work on this metal, and the study is extended to cobalt and nickel from 0 to 1500 volts and to copper from 0 to 90 and 700 to 1200 volts.

<sup>1</sup> Thomas, Phys. Rev. 25, p. 319 (1925).

## RESULTS AND DISCUSSION

Critical potentials were determined from the positions of breaks which were found in the curves obtained when the ratio of the photo-electric to the thermionic current was plotted as a function of the voltage applied between the hot filament cathode and the target anode. This voltage was corrected for initial velocity, and contact difference of potential, and to it was added the "work function"  $\phi$  of the metal, according to the relation  $h\nu = e(V + \phi)$ , from which the radiation frequencies may be computed. Two types of breaks have been observed and are designated as radiation (*R*) and ionization (*I*) potentials, following the analogy in the case of similar breaks observed when gases instead of metals are studied. The *R* breaks are followed by a portion of the curve which is concave downward

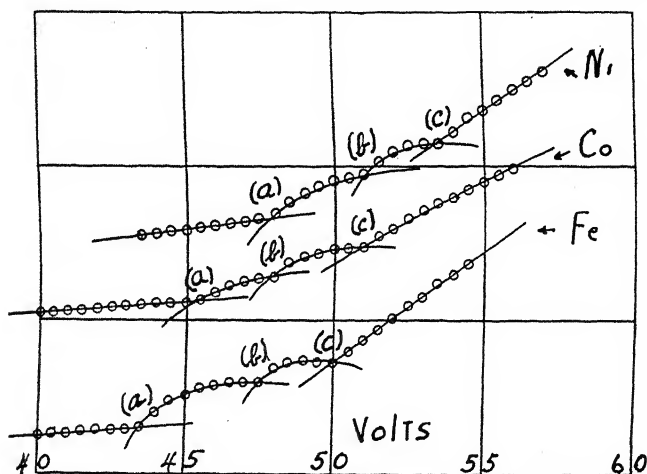


Fig. 1. Curves showing the progression with atomic number in the corresponding critical potentials of Fe, Co and Ni. Breaks *a* and *b* are of type *R*, while *c* is of type *I*. These breaks, and those in Fig. 2, have been exaggerated by plotting as ordinates the differences between the experimental points and points on a straight line of convenient slope.

and the *I* breaks are followed by portions of the curve which are straight or slightly concave upward. The designation may not correspond to the true physical facts, but is convenient as a basis of classification.

In the previous paper the reproduction of the curves was somewhat disappointing as regards the definiteness with which the breaks were shown. This was due to the fact that the change of slope was never large and often required careful examination to locate it. In order to bring out breaks more convincingly, the differences between the actual curves and straight lines of convenient slope have been plotted in Figs. 1 and 2. In

this manner no spurious breaks are introduced, but the actual breaks can be magnified so as to be as evident as desired. It should be said, however, that all actual locations of breaks were made from the original observations, plotted on large scale.

Fig. 1 shows typical curves, thus replotted. The curve for iron shows three breaks of which *a* and *b* are of the *R* type and *c* is of the *I* type. The curves for cobalt and nickel are very similar but with each break displaced toward higher voltages with increasing atomic number. This similarity, with the regular displacement, is apparent for the entire range 0 to 1500 volts.

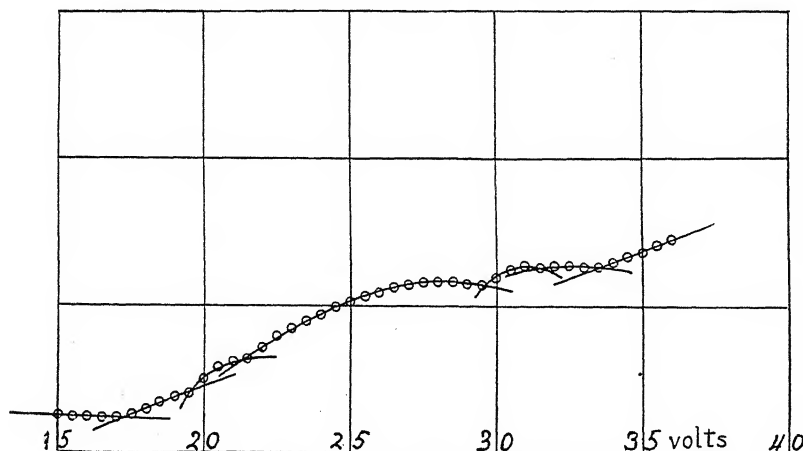


Fig. 2. Critical potentials of copper in the range 15 to 35 volts (uncorrected), as shown by a single run. Such curves were accurately reproduced in numerous check runs.

Fig. 2 is a replotted curve for copper. All the breaks shown are reproducible, appearing on all curves taken over this range. The break at 31.5 volts might be considered as questionable from this curve alone, but its appearance on other curves, especially those taken at smaller voltage intervals, indicates that it is genuine. In this connection it may be mentioned that more than 100 independent curves were obtained for each of the metals Fe, Co and Ni, and that the breaks here reported were consistently shown.

In several previous papers<sup>2,3,4,5</sup> on the photo-electric determination of critical potentials by essentially the same method, but with less sensitive

<sup>2</sup> Kurth, Phys. Rev. **18**, p. 461 (1921).

<sup>3</sup> Horton, Andrewes and Davies, Phil. Mag. **46**, p. 721 (1923).

<sup>4</sup> Miss Levi, Trans. Roy. Soc. Canada **18**, p. 159 (1924).

<sup>5</sup> Holtsmark, Phys. Zeits. **23**, p. 252 (1922); **24**, p. 225 (1923).

apparatus in which a considerably less proportion of the radiation was intercepted by the detecting electrode, previous authors have reported from one to four critical potentials in the range wherein the present work has shown 46 or 48. In order to illustrate the cause of this difference, the results of the present investigation were plotted at larger voltage intervals and the best lines drawn through these points. Fig. 3 shows such a curve for nickel, at two volt intervals. The curve shows breaks at 82 and at 104 or 110 volts, or both. In this range Miss Levi<sup>3</sup> has reported breaks at 76.8 and 102.8 volts; Horton et al.<sup>2</sup> found 104 volts; Holtzmark<sup>4</sup>

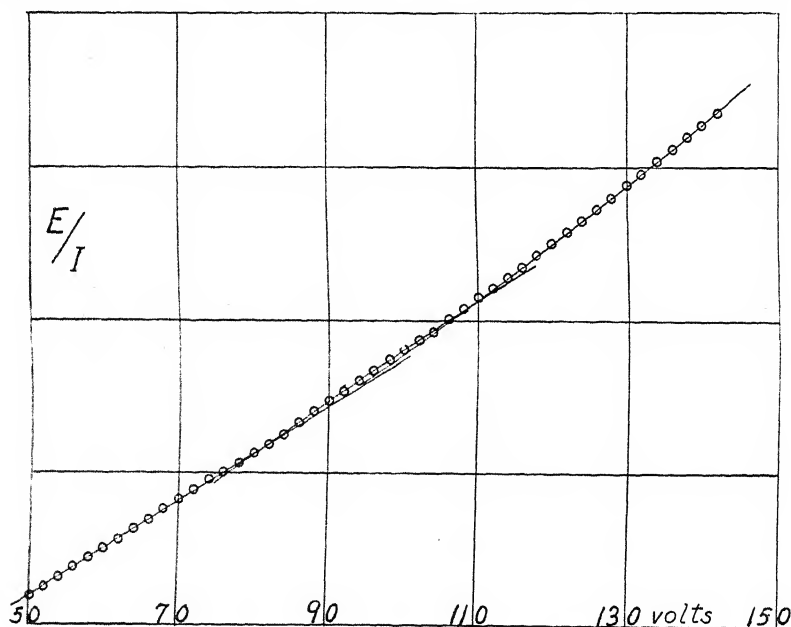


Fig. 3. Shows the result of plotting a larger range 50 to 150 volts at 2 volt intervals. The multiplicity of breaks is no longer visible, but there are points at which the slope of the curve changes, at 82 and at 104 or 110 volts. These points are identified with the critical potentials reported by previous observers.

reported 117.7 volts. These results, all uncorrected for work function, are in as good agreement as could be expected, since a break could not be located on a curve such as Fig. 3 without a possible error of two volts. It seems quite probable that the discrepancies between these values of the several investigators lie within the limits of accuracy of the several experiments. The same sort of agreement has been found in the other ranges and with both copper and iron also, insofar as these have been tested in this way. In the entire range 0 to 1500 volts for nickel, for instance, only four breaks stand out as permanent, considerable changes in

slope, and the curve is readily reconciled with Miss Levi's latest values of 53.6, 76.8, 102.8, 355.1 and 781.3 volts as the critical potentials. In the present work, however, 46 breaks appeared in curves which were reproducible when plotted to the full sensitivity of the apparatus and at small voltage intervals. We therefore conclude that the breaks shown by the present work are real and significant and that the failure of some previous investigators to discover them is due to lack of resolving power of their apparatus, resulting from lack of sensitivity or steadiness or the failure to take observations at sufficiently small voltage intervals. The present results are therefore not in conflict with previous work, but constitute an extension of it.

The potential drop across the filament, which consisted of several turns of helically wound tungsten wire, was from 2 to 2.6 volts, depending on its temperature. When the lead loss of about 1.25 volts is subtracted, there is left a potential range of from 0.75 to 1.35 volts over which the electrons are emitted. Taking the middle point of the filament as the source of electrons, making corrections for the contact difference of potential between the filament and the target, and allowing for the average initial energy of emission, it was estimated that the net correction amounted to 1.0 volt which should be subtracted from the applied voltage. To this was added the work function  $\phi$ , which has been taken as 5.0 volts for all the elements used, as explained in the preceding paper. These corrections are believed to be correct to  $\pm 0.2$  volt, exclusive of the uncertainty in the value of  $\phi$ .

Table I gives the assembled results of the present investigations. At the head of the table are equations whereby the results may be converted into equivalent wave-lengths (in angstrom units) or into values of  $\nu/R$ . The *I* or *R* following the value for the intensity *J* indicates the type of break. The voltages marked ? are doubtful breaks, since the breaks did not appear on every curve. *I* or *R* is followed by ? in each case in which it was difficult to classify the break, because it did not have the same shape on every curve. Except for the cases so marked, it is believed that the experiments are conclusive on the results as stated. In the case of iron the break at 159.8 volts replaces the one previously reported at 158.5, which was later found to be in error.

In order to show clearly the relation between these critical potentials of the several metals, they are plotted in Figs. 4 and 5. In Fig. 4 the position and relative intensity of the nine breaks of the *I* type are plotted for iron, cobalt and nickel. The corresponding lines show a general agreement in intensity and an excellent agreement in position, for, in accordance with the Moseley law, each corresponding line is displaced



TABLE I

*Critical potentials for Fe, Co, Ni and Cu.*  
 $V$  = critical potential,  $J$  = intensity,  $\lambda = 12354/V$ ,  
 $I$  = ionization break;  $R$  = radiation break;  $\nu/R = V/13.56$ .

Fe		Co		Ni		Cu	
$V$	$J$	$V$	$J$	$V$	$J$	$V$	$J$
7.3	2.5 R	8.8	1.2 R	8.6	2.4 R	10.3	2.3 R
11.1	2.7 I	11.6	3.5 I	11.7	4.0 I	12.3	3.4 I
14.1	2.2 R	14.4	2.5 R	14.6	2.0 R	14.2	2.4 R
16.5	2.9 R	17.0	3.1 R	18.0	2.4 R	15.7	2.0 R
19.4	1.8 I	20.9	2.3 I	22.2	2.3 I	19.0	2.3 I
24.3	1.3 R	25.7	1.8 R	27.3	1.6 R	20.7	1.4 R
28.8	2.5 R	29.3	1.2 R	31.0	1.4 R	23.8	1.8 R
34.3	2.0 R	32.2	2.2 R	34.6	2.2 R	25.5?	1.4 R
37.5	1.1 R	38.5	1.9 R	39.8	1.4 R	33.7	1.8 R
41.2	2.5 I	43.2	1.6 I	44.7	1.5 I	35.5?	0.8 R
48.0	2.4 R	49.3	1.8 R	51.3	2.0 R	37.5	2.8 R
51.3	1.6 R	52.8	1.2 R	54.8	0.9 R	40.0	1.2 R?
54.6	3.1 I	55.8	2.9 I	57.4	3.1 I	42.0	1.8 R
62.0	2.7 R	62.8	1.7 R	65.6	2.0 R	45.9	1.2 I?
67.6	1.6 R	70.7	1.1 R	71.9	1.5 R	49.0	0.9 R
75.3	2.2 R	76.7	1.8 R	79.8	1.7 R	51.0	1.9 R
...	...	81.0	1.2 R	...	...	53.8	2.2 R
82.7	2.3 R	84.3	1.9 R	87.2	1.6 R	62.0	1.8 R
87.0?	1.1 R	89.4?	1.3 R	91.2?	0.9 R	64.5	1.6 R
91.2?	1.3 R	92.5?	1.5 R	94.9?	1.2 R	74.0	1.6 R
94.8	1.3 R	97.7	1.7 R	98.3	1.7 R	84.0	1.8 R
103.5	2.0 I	104.4	2.0 I	106.5	2.0 I	88.0	1.4 R
112.2	1.7 R	114.3	1.9 R	116.6	1.2 R		
125.7	1.5 R	125.5	1.3 R	127.0	1.0 R		
131.8	1.9 R	131.4	1.5 R	133.7	1.4 R		
136.0	1.3 R	138.3	1.5 R	139.6	1.4 R		
140.7	1.6 R	143.8	1.5 R	145.0	1.3 R		
150.2	1.6 R	154.0	1.3 R	156.8	1.4 R		
159.8	1.3 R	163.5	1.3 R	167.3	1.0 R		
169.4	2.3 I	173.3	1.3 I	178.2	1.2 I		
181.6	1.2 R	185.5	1.2 R	186.2	1.2 R		
192.0	1.8 R	195.6	1.6 R	197.7	1.8 R		
212.0	1.5 R	214.0	1.3 R	217.7	1.3 R		
221.3	1.1 R	223.0	1.4 R	228.2	1.1 R		
228.1	2.8 I	230.8	1.9 I	232.7	1.8 I		
241.0?	1.0 R	244.8	1.1 R	247.7	1.3 R		
250.8	1.4 R	255.5	1.5 R	257.0	1.6 R		
261.5	1.1 R	264.6	1.3 R	265.9	1.4 R		
271.5?	1.2 R	277.4	1.8 R	280.0	2.0 R		
277.4	1.4 R	285.1	1.5 R	286.5	1.4 R		
288.6	1.1 R	293.7	1.2 R	294.9	0.9 R		
303.7	1.8 R	306.5	2.1 R	311.5	1.8 R		
...	...	326.3	1.2 R	...	...		
331.0	1.6 R	335.8	2.3 R	341.3	2.0 R		
639.0	0.9 R	705.2	1.1 R	774.0	0.9 R	820.4	1.4 R
704.3	1.5 I	764.8	1.8 I	833.4	2.1 I	929.0	2.2 I
818.5	2.0 I	873.2	2.0 I	948.0	2.0 I	1017.0	2.0 I
...	...	950.1?	1.3 R	1017.3	0.7 R		

toward higher voltages with increasing atomic number, the amount of the displacement increasing with the voltage. This agreement in displacement is a strong support for the validity of these results, and their interpretation as indicating the excitation of soft x-rays. Fig. 5 similarly

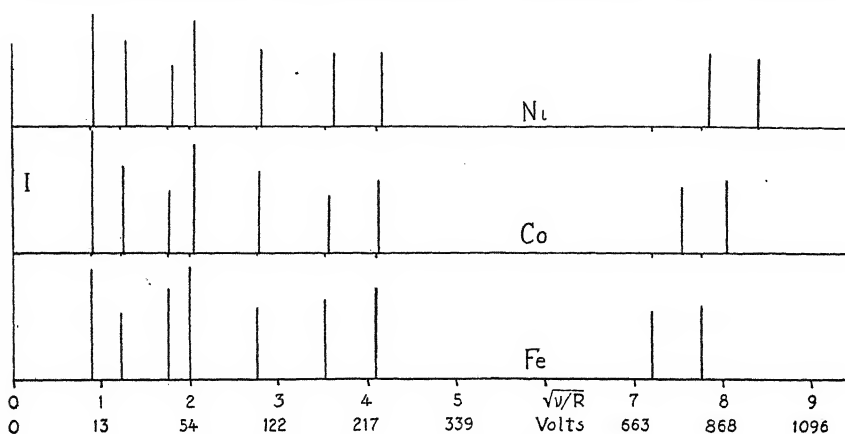


Fig. 4. Type I breaks plotted to a scale of  $\sqrt{v/R}$ . Lengths are proportional to intensities of breaks. Dots on the axes for Co and Ni indicate the location of the Fe breaks, so as to bring out the displacement with atomic number.

represents the  $R$  potentials up to 350 volts. Here, likewise, there is an evident correspondence and a regular displacement of the breaks in the case of iron, cobalt and nickel, but there is no obvious agreement in the case of copper. The lowest voltage break in each case could not be determined as accurately as the others. The next one, shown as a dotted line, is an  $I$  potential, and shows good agreement for all four metals.

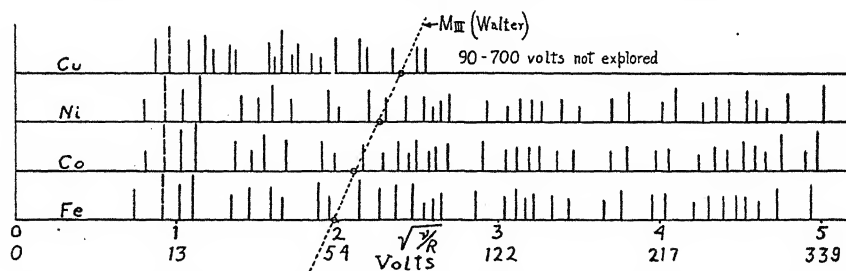


Fig. 5. Type R breaks plotted to a scale of  $\sqrt{v/R}$ . The dotted line shows the positions of the  $M_{III}$  critical potentials as calculated from the combination principle.

Cobalt shows two more breaks than does iron or nickel. The corresponding breaks were not certainly established for the latter metals, although there was a suggestion of these breaks on some of the curves. The fact that cobalt was used last, when the experimental technique had

been improved, possibly accounts for the location of these two extra breaks. The break at 34.3 volts in iron is not in good agreement with the corresponding breaks for cobalt and nickel. Careful check runs failed to detect any error in the determination of this voltage, so that the peculiarity seems to be real.

It is probable that the failure of the critical potentials of copper to correspond with those of the other metals in the lower voltage range is to be explained on the basis of the Bohr theory. Iron, nickel and cobalt form a transition group in which the outer electron configuration is probably similar in all three and the configuration is in a somewhat

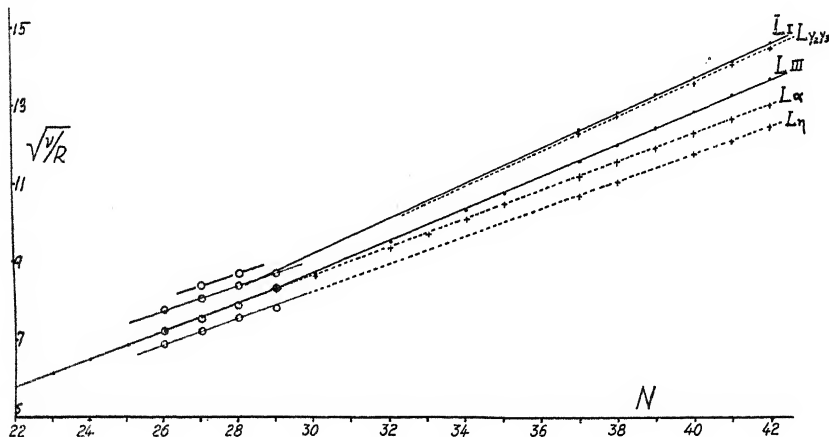


Fig. 6. Moseley diagram showing critical potentials of the L series. Circles represent results of the present investigation. Other points are taken from x-ray spectroscopic data.\*

labile state. In copper these groups are believed to exist in definite stable configurations. In support of this belief is the fact that the Moseley curves show changes of slope between nickel and copper, as is illustrated by the curve  $L_{III}$  in Fig. 6.

In attempting to correlate these critical potentials with spectroscopic data of x-rays, it must be born in mind that the only x-ray data which have been obtained for this spectral region are values of the  $L_{III}$  absorption limits, which have been computed from K series data by Walter<sup>6</sup> and Bohr and Coster<sup>7</sup> and others. Emission data for the  $L_{\alpha}$  line are given for elements down to (including) copper by Hudson<sup>8</sup> and by Siegbahn

<sup>6</sup> Walter, Zeits. f. Phys. 30, 350 (1924).

<sup>7</sup> Bohr and Coster, Zeits. f. Phys. 9, 286 (1924).

<sup>8</sup> Hudson, J. Opt. Soc. Am. and Rev. Sci. Inst. 9, 286 (1924).

\* Values of Siegbahn and Thoreäus are not plotted.

and Thoræus<sup>9</sup> for the  $L\alpha$  and  $L\beta$  emission lines for the elements Cu, Ni Co and Fe. The Moseley curves can be drawn through this region for the L series only by extrapolation or by calculations based on the combination principle which are of limited accuracy. Fig. 6 shows the x-ray data<sup>10</sup> in this spectral region together with the data which have been obtained from the present investigation.

One of the critical potentials of type *I* for each metal is seen to agree almost exactly with the  $L_{III}$  spectral term. The other *I* critical potential comes where we might expect the  $L_I$  term to be, as shown by the extrapolated line. Both of these sets of potentials show the change of slope of the Moseley curves between nickel and copper. The lowest critical potential of type *R* for each metal is in about the right place to be identified with the  $L\eta$  emission line. The highest *R* potentials, observed only in cobalt and nickel, cannot at present be identified with any term of the spectrum. The values of Siegbahn and Thoræus for the  $L\alpha$  line agree within 1.5 percent with the author's values designated as  $L_{III}$ . The average of the  $L\alpha$  and  $L\beta$  lines by Siegbahn and Thoræus for each of these four elements shows equally good agreement with the corresponding values for  $L_{III}$ . This shows that the present method is not capable of differentiating between the lines  $L\alpha$ ,  $L\beta$  and the absorption limit  $L_{III}$ . Taken as a whole, there seems to be little room for doubt that these higher critical potentials are definitely associated with x-ray terms of the L series. Table II gives values of  $\nu/R$  for  $L_{III}$  as given by Walter,<sup>8</sup> by Bohr and Coster<sup>7</sup> and as calculated from the present work, together with the values of  $L\alpha$  by Siegbahn and Thoræus.<sup>9</sup>

TABLE II  
Values of  $\nu/R$  for  $L_{III}$  and  $L\alpha$

	Authority	Fe	Co	Ni	Cu
For $L_{III}$	Walter	52.19	57.5	63.1	69.09
	Bohr and Coster	52.2	58.5	61.3	69.8
	Thomas	52.01	56.46	61.52	68.58
For $L\alpha$	Siegbahn and Thoræus	51.63	56.73	62.23	68.09

Not much can be said with certainty regarding the M terms. The only one of these which is given with any assurance is the  $M_{III}$  term, determined by the combination principle by Walter, and shown by the dotted line in Fig. 5. Probably the M terms would appear at voltages between

<sup>9</sup> Siegbahn and Thoræus, *Arkiv f. Matematik, Astron. och Phys.* **18**, No. 24 (1924).

<sup>10</sup> Values of Siegbahn and Thoræus are not plotted.

100 and 200, and the remaining M terms, together with the N, etc., terms, would be below 50 volts. This leaves a number of the critical potentials which seem to be too high to fit into the M scheme, but are quite definitely related to these rather than to the higher L terms.

It scarcely seems worth while to hazard an explanation of these numerous lower critical potentials, but three possibilities may be kept in mind. (1) Some of the critical potentials may be due to "multiple excitation"; that is, an electron may lose just enough energy to one atom to excite some type of radiation and retain just enough to excite another atom also. Such double excitation should give critical potentials which are the sum of others associated with single excitation. (2) Some of the critical potentials may be associated with the x-ray spark lines, which are unknown in this part of the spectrum but which must certainly be present. (3) It may be that the permanent changes in slope of the curves, such as are found when less resolving power is used, are the breaks which correspond to the x-ray terms. As mentioned earlier in the paper, such changes, in the case of nickel, occur at 82, 104 or 110 as well as 833 and 948 volts. It is possible to identify all these with  $M_{III}$ ,  $M_I$ ,  $L_{III}$  and  $L_I$  respectively.

In order to arrive at a satisfactory correlation and explanation of such critical potentials as are reported in this paper, it is desirable to make similar observations on metals of lower atomic number where the spectral relations should be simpler, and also on elements of higher atomic number whose x-ray relations have been more completely worked out. Such work is now in progress.

In conclusion, the writer wishes to express his thanks to Professor K. T. Compton for his encouragement and for his most helpful assistance during the course of this investigation.

PALMER PHYSICAL LABORATORY,  
PRINCETON, N. J.  
August 18, 1925.

APPLICATION OF THE CORRESPONDENCE PRINCIPLE TO  
RELATIVE INTENSITIES IN SERIES SPECTRA

BY FRANK C. HOYT

## ABSTRACT

A brief discussion is given of the representation of intensities in emission and absorption in terms of the probabilities of transition and of the estimation of the probability  $A'_{\nu}$  of spontaneous transition in the usual way based on the correspondence principle. It is shown that on the basis of the Bohr theory approximate values of  $A'_{\nu}$  may be obtained in many cases from the information as to the parameters of the stationary orbits which is given by the values of the spectral terms and their quantum numbers, together with the harmonic analysis of the penetrating orbits given in a previous paper.<sup>1</sup> In other cases a detailed knowledge of the intermediate orbits is shown to be necessary. Calculations are made of the *relative probabilities of the transitions involved in the principal series of sodium*. The values obtained by different methods of averaging are compared with the experimental results of Harrison (Phys. Rev. 25, 768, 1925). A possible explanation is offered of the observed relative intensities in emission of certain lines with the same initial state. It is pointed out that the frequencies of the spectral lines may be approximately calculated from the orbital frequencies of the series electron when the orbits are similar as in the case of *sp* combinations.

## 1. INTRODUCTION

IN a previous paper<sup>1</sup> a method was given for obtaining an approximate harmonic representation of the so-called orbits of the second kind or penetrating orbits of the electrons in the atom, based on the atomic theory of Bohr. In the present paper a brief discussion will be given of the application of the correspondence principle to the estimation of relative intensities in emission and absorption, followed by an outline of the way in which the analysis of the previous paper may be applied to line spectra. No data at present available on emission intensities appear to be sufficiently reliable for a comparison with the theoretical predictions, but in the case of some recent measurements on intensities in absorption in the principal series of sodium a quantitative comparison will be made with the calculations.

2. THEORY OF THE ESTIMATION OF THE INTENSITIES OF SPECTRAL LINES  
ON THE BASIS OF THE CORRESPONDENCE PRINCIPLE

We shall assume that the intensity  $I$  in emission of a spectral line of frequency  $\nu$  is given by the expression

$$I = N' A'_{\nu} h \nu \quad (1)$$

<sup>1</sup> F. C. Hoyt, Phys. Rev. 25, 174 (1925). In what follows the results and notation of this previous paper will be used.

where  $N'$  is the number of atoms present in the initial state,  $h$  is Planck's constant and  $A'_{,,}$ , the probability as introduced by Einstein<sup>2</sup> that a given atom undergo in unit time a spontaneous transition from one stationary state indicated by a single prime to one of lesser energy indicated by a double prime.<sup>3</sup> An estimate of the probability  $A'_{,,}$  may now be made on the basis of the correspondence principle in the well-known way<sup>4</sup> if the rate of emission of energy given by (1) is equated to that of an equivalent harmonic oscillator radiating according to the classical laws. This gives

$$A'_{,,} = \frac{1}{h\nu} \frac{32\pi^4 e^2}{3c^3} (Q^2 \nu_0^4) \quad (2)$$

where  $Q$  is the effective amplitude and  $\nu_0$  the effective frequency of the equivalent or "virtual" oscillator. The fact that the frequency  $\nu$  may be represented for multiply periodic systems as an average value of the "corresponding" harmonic  $\omega_0 = \tau_1 \omega_1 + \dots + \tau_s \omega_s$  by an expression of the form

$$\nu = \int_0^1 \omega_0 d\lambda \quad (3)$$

where  $\lambda$  is a parameter defining a set of states intermediate between the initial and final states, suggests that  $(Q^2 \nu_0^4)$  may also be obtained from an average value of the same type of the quantity  $C^2 \omega_0^4$  or of some function of this quantity, where  $C$  is the resultant amplitude of the corresponding harmonic component of the electric moment of the atom.<sup>5</sup>

A great variety of possible types of average<sup>6</sup> have been suggested but their evaluation is possible only in the simplest cases. However, in certain instances a sufficiently accurate estimate of  $A'_{,,}$  may be obtained by representing  $Q$  as a simple average of its values in the initial and final stationary states, as for example by

$$Q^2 = \frac{1}{2} (C'^2 + C''^2) \quad (4)$$

with

$$\nu_0 = \nu$$

in which case

$$A'_{,,} = \left( \frac{32\pi^4 e^2}{3c^3 h} \right) Q^2 \nu^3$$

<sup>2</sup> A. Einstein, *Phys. Zeits.* **18**, 121 (1917).

<sup>3</sup> In what follows quantities referring to the state of greater energy will always be denoted by a prime, while those referring to the state of lesser energy will be denoted by a double prime.

<sup>4</sup> See, for example, Ladenburg and Reiche, *Naturwissenschaften* **11**, 584 (1923).

<sup>5</sup> N. Bohr, *Zeits. f. Physik* **13**, 142 (1923).

<sup>6</sup> For a brief discussion of the possible types of average see F. C. Hoyt, *Phil. Mag.* **46**, 135 (1923).



and from Eq. (1)

$$I = \text{const.} \times Q^2 \nu^4. \quad (5)$$

We must remember, however, that in many cases it will be necessary to take into account the amplitudes  $C$  in the intermediate states. Such will in general be the case when these amplitudes differ greatly from those in the stationary states, and a certain criterion for the applicability of so simple an average as Eq. (4) may be found in the possibility of representing the frequency  $\nu$  with sufficient accuracy by an average of the type

$$\nu = \frac{1}{2}(\omega_0' + \omega_0'') \quad (6)$$

involving only the orbital frequencies in the stationary states.

### 3. THE ESTIMATION OF THE CORRESPONDING AMPLITUDES

In the previous paper a brief discussion was given of the character of the electron orbits involved in the emission of line spectra and the method of estimating the corresponding amplitudes was outlined. Here we shall consider in more detail the determination of these amplitudes in simple cases, using the results and notation of that paper. It is assumed that to a high degree of approximation the motion of the series electron may be regarded as a central motion, and hence the stationary states may be designated by the quantum symbol  $n_k$ , where  $n$  is the principal quantum number and  $k$  the subordinate quantum number. The value of the given spectral term is then a function of  $n$  and  $k$  and the terms may be arranged in series, each series corresponding to a certain value of  $k$  and the terms within a given series being approximately representable by a Rydberg formula with successive integral values of  $n$ . In the case of the simple systems of series occurring in a large number of elements the values of the terms are given by series expressions

$$m\iota = p^2 R / (n - q_i)^2 \quad (7)$$

where the  $q$ 's, which are ordinarily called the quantum defects, are to a first approximation independent of  $n$ . Here  $p$  is the degree of ionization of the atom (i.e.  $p$ , which is the same as the  $N - N_i$  of the previous paper, is 1 for the arc spectra, 2 for first spark spectra, etc.). The integer  $m$  is merely the serial number of the term and is not to be confused with the quantum integer  $n$ , while  $\iota$  stands for any one of the characteristic term series  $s, p, d, f, \dots$  for which  $k = 1, 2, 3, 4, \dots$  respectively.

The values of the  $k$ 's for the various series are readily assigned from simple considerations, but the fixation of the principal quantum numbers  $n$  is a matter of greater difficulty. Obviously the quantum defects will be dependent on the values of  $n$ , as the denominator  $(n - q)^2$  only is

fixed by the value of the term. Assuming any assignment of the  $n$ 's, however, we have the following approximate method of finding the corresponding amplitudes.

According to the formula derived in the previous paper the amplitudes  $C_\tau$  of the circular vibrations

$$x + iy = \sum_{-\infty}^{+\infty} C_\tau e^{2\pi i(\tau\omega + \sigma)t}$$

into which the motion of the series electron referred to axes in the plane of the orbit may be resolved, are represented for a given value of  $\tau$  as

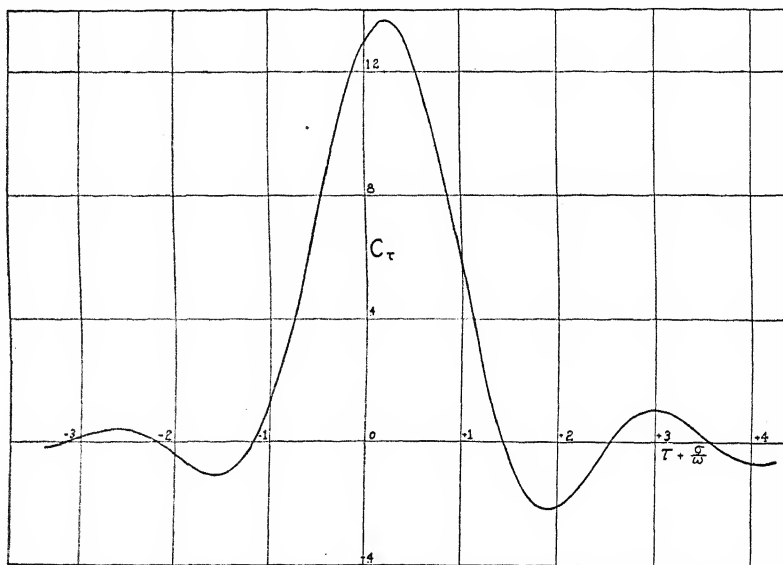


Fig. 1. Plot of  $C_\tau/a$  as a function of  $\rho = \tau + \sigma/\omega$  for  $\epsilon = .8660$ .

functions of the major axis  $a$ , the eccentricity  $\epsilon$  of the outer loop, and the quantity  $\sigma/\omega$  which for the penetrating type of orbit assumed is equal to the ratio of the frequency of precession to the radial frequency of the motion. The coefficients are of course directly proportional to the major axis. It will be seen from Eq. (22) of that paper, however, that in reality the amplitudes for given values of  $a$  and  $\epsilon$  are continuous functions of the quantity  $\rho = \tau + \sigma/\omega$  in the case of penetrating orbits.<sup>7</sup> Fig. 1 shows the computed values of  $C_\tau/a$  plotted as a function of  $\rho$  for  $\epsilon = .8660$ , the eccentricity of a  $2_1$  orbit in hydrogen. This plot may then be interpreted in two ways. If we consider only values of  $\sigma/\omega$  between 0 and 1 the portion

<sup>7</sup> For orbits of the non-penetrating type the coefficients  $C_\tau$  are given to a first approximation by Eq. (22) with  $\sigma/\omega = 0$ .

of the curve from  $\rho=0$  to  $\rho=1$  represents  $C_0$  as a function of  $\sigma/\omega$  while that from  $\rho=1$  to  $\rho=2$  represents  $C_1$  as a function of  $\sigma/\omega$ , and so on. If, however, we consider values of  $\sigma/\omega$  greater than 1 as seems to be necessary in certain cases, we may think of the whole curve for positive  $\rho$  as representing  $C_0$  as a function of  $\sigma/\omega$ , or by proper shift of the origin as giving any  $C_r$  as a function of  $\sigma/\omega$ . For the actual estimation of the amplitudes by graphical interpolation a plot of  $C_r$  as a function of  $\epsilon$  for discrete values of  $\sigma/\omega$  is more convenient, but the diagram given here shows more clearly the effect of increasing rotation on the coefficients. The character of the curve does not depend greatly on the value of  $\epsilon$  if  $\epsilon$  is near 1. For  $\epsilon=1$  the curve is symmetrical with respect to the vertical axis.

From a consideration of spectral data alone it is possible to estimate the value of  $C_r$  corresponding to an assignment of the  $n$ 's and  $k$ 's to the various terms, as these data give approximate values of  $\epsilon$ ,  $a$ , and  $\sigma/\omega$ . As already pointed out  $\tau$  is given by the changes in the quantum numbers. Thus  $\tau = \pm \Delta n$ , the positive sign being taken if it changes in the same sense as  $k$  and the negative sign being taken if it changes in the opposite sense.<sup>8</sup> The quantities  $a$  and  $\epsilon$  may be found in the well-known way from the effective quantum numbers by means of Eqs. (7), (8), and (9) of the previous paper. The values of  $\sigma/\omega$  can be estimated as follows<sup>9</sup>: From the general theory of multiply periodic systems the values of  $\omega$  and  $\sigma$  satisfy the relations  $\omega = \partial E / \partial J$ ,  $\sigma = \partial E / \partial P$  where  $J$  and  $P$  are the "uniformization variables" conjugate to  $\omega$  and  $\sigma$  respectively. Since in the stationary states  $J = nh$  and  $P = kh$  we have,

$$\omega = \frac{1}{h} \frac{\partial E}{\partial n}, \quad \sigma = \frac{1}{h} \frac{\partial E}{\partial k} \quad (8)$$

where  $E$  is the total energy of the motion. If we suppose this energy to be given by the formula

$$E = Rh / (n - q)^2$$

we get by carrying out the differentiation, remembering that  $q$  depends only on  $k$ ,

$$\sigma/\omega = -dq/dk. \quad (9)$$

Thus  $\sigma/\omega$  is given approximately by the negative of the slope of the curve obtained by plotting  $q$  as a function of  $k$  for a constant value of  $n$ . It must be remembered that the values of  $q$  depend on the  $n$ 's, and consequently the values of the corresponding amplitudes depend on the

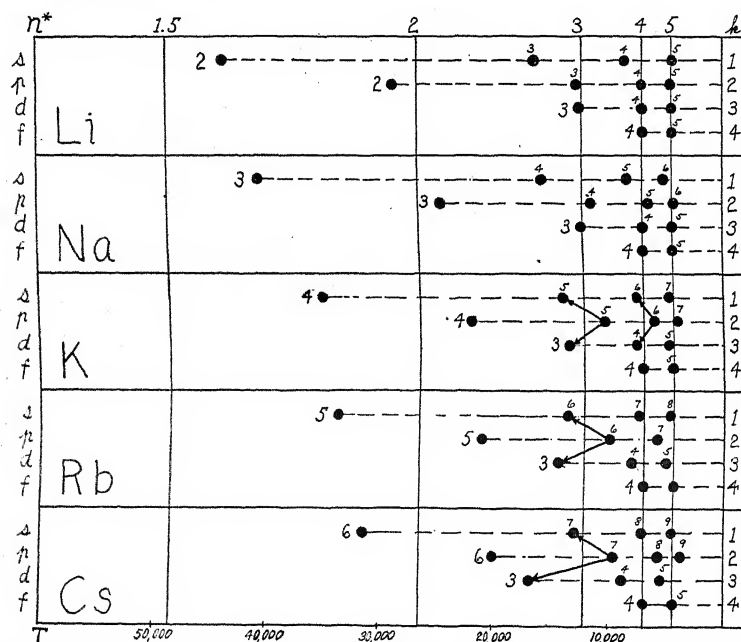
<sup>8</sup> See p. 184 of the previous paper.

<sup>9</sup> See Thomas, Zeits. f. Phys. 24, 169 (1924).

assignment of the principal quantum numbers not only through the order of the harmonic but also through the values of  $\sigma/\omega$ .

#### 4. CALCULATION OF TRANSITION PROBABILITIES FOR THE ALKALI METALS

In this section we shall discuss the application of the general considerations outlined above to some special types of transition in the arc spectra of the alkalis and give the quantitative results for the principal series transitions of sodium.



ponents. Such a procedure cannot be strictly justified and in fact as pointed out by Kemble<sup>10</sup> and others the transition probability in such a case of degeneracy may be expected to depend in some way on the statistical weights of both initial and final states. It should be noted, however, that in comparing relative probabilities of transition of lines of the same series within which the statistical weights of initial and final states are the same, the existence of such a factor would not influence the results. In comparing lines of different series, however, it would probably have to be taken into account.

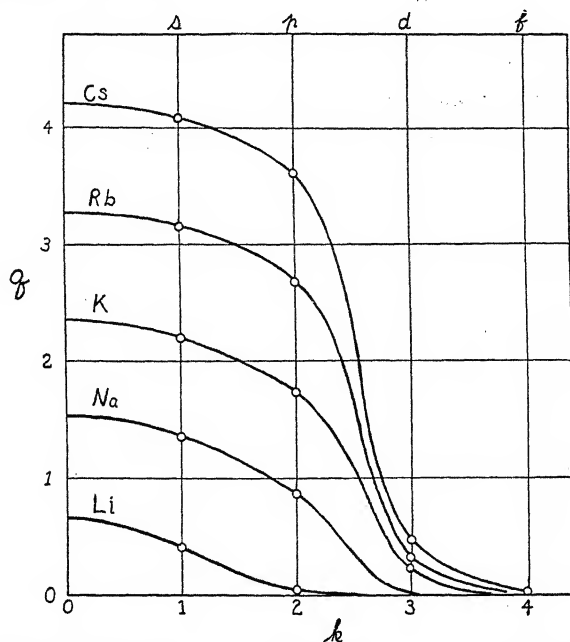


Fig. 3. Plot of the quantum defect  $q$  (cf Eq. (7)) as a function of  $k$  for the arc spectra of the alkalis.

The values of  $\sigma/\omega$  for the  $s$  and  $p$  states necessary for the estimation of the corresponding amplitudes as determined from Eq. (9) by means of a plot of the quantum defect  $q$  against  $k$  for constant  $n$  (Fig. 3) are given in Table I. The variations of  $q$  with  $n$  have been neglected, as they are small compared to the uncertainties in drawing the curves and finding the slopes. For the  $d, f, \dots$  terms we may suppose that the values of  $\sigma/\omega$  are zero or at any rate very small, as according to Bohr<sup>11</sup> they are due to orbits of the non-penetrating type, while the  $s$  and  $p$  terms are due to orbits of the penetrating type.

<sup>10</sup> E. C. Kemble, Phys. Rev. **25**, 1 (1925).

<sup>11</sup> N. Bohr, Ann. der Phys. **71**, 228 (1923).

Values of the corresponding amplitudes in the stationary states may now be found for any desired transition, as described in Section 3. For this purpose plots of  $C_r$  as a function of  $\epsilon$  for different values of  $\sigma/\omega$  were found most convenient. In estimating the transition probabilities, how-

TABLE I

*Values of  $\sigma/\omega$  in the  $s$  and  $p$  states.*

Element	$s$ states	$p$ states
Na	.35	.70
K	.31	.67
Rb	.29	.86
Cs	.28	1.00

ever, some consideration must be given to the probable values of the amplitudes in the "intermediate" states. In fact, as pointed out in Section 2, it is only in certain cases that we can hope to represent these probabilities in terms of the amplitudes in the stationary states alone, and a reasonable criterion for the possibility of representing the probabilities in this way may be found in the degree of approximation with which the frequency  $\nu$  may be represented as an average of the type of Eq. (6), involving only the corresponding orbital frequencies in initial and final states.

TABLE II

*Comparison of computed and observed frequencies.*

Element	Line	Calc. (1)	Calc. (2)	Obs.	$\sigma/\omega$
Na	$2s-3p$	4590		4529	
	$3d-3p$	5330	1170	1093	.856
K	$2s-3p$	3660		3683	
	$3d-3p$	13680	3900	3179	1.51
K	$3s-4p$	1550		1550	
	$4d-4p$	4780	1730	1611	1.51
Rb	$2s-3p$	3940		3660	
	$3d-3p$	21900	5270	4437	2.35
Rb	$3s-4p$	1720		1553	
	$4d-4p$	9350	2260	2164	2.35
Cs	$2s-3p$	4050		3410	
	$3d-3p$	25000	8040	7348	3.15

Calc. (1) : Frequencies computed from the equations  $\nu = \frac{1}{2}(\omega_0' + \omega_0'')$ ;  $\omega_0 = (\tau + \sigma/\omega)$  ( $2R/n^3$ ).

Calc. (2) : Frequencies computed from the equation  $\nu = (\tau + \sigma/\omega)\bar{\omega}$  where  $\bar{\omega}$  is the slope of the straight line joining the stationary states in Fig. 3 and  $\bar{\omega} = \frac{1}{2}(\omega' + \omega'')$ . Values of  $\sigma/\omega$  used are given in the last column.

If we apply this criterion to the transitions involved in the alkali spectra we find that for transition between  $s$  and  $p$  terms the frequencies may be represented with a fair degree of accuracy by Eq. (6). For  $pd$  combinations, on the other hand, Eq. (6) does not give even a first approximation. The results of computations of the frequencies for certain  $sp$  and  $pd$  combinations are shown in the first column of Table II. The frequencies  $\omega_0 = \tau\omega + \sigma = (\tau + \sigma/\omega)\omega$  of the corresponding harmonics have been found from the values of  $\sigma/\omega$  in Table I and values of  $\omega$  computed from the spectral terms by means of the relation  $\omega = 2R/n^{*3}$ . In the second column are given values of  $\nu$  computed from the harmonic of an intermediate orbit for which  $\sigma/\omega$  is taken as the slope of a straight line joining the stationary states in Fig. 3. In this case the agreement is better, although not quantitative.

This difference between  $sp$  and  $pd$  combinations is probably due to the fact that the former are transitions between orbits both of which are of the same type (penetrating orbits) while the latter are transitions between penetrating and non-penetrating orbits, in which case one may expect very large values of the frequency of precession when the series electron penetrates almost tangentially into the inner region.

We may then conclude that for  $sp$  combinations the transition probabilities may be approximately represented by an average of corresponding amplitudes in the stationary states. Computations have been made for various transitions, but it is only in the case of the principal series of sodium that a satisfactory comparison with experimental data seems possible at present, and hence only the results for these transitions are reproduced here. Table III gives the computed corresponding amplitudes necessary for a calculation of the transition probabilities for the first five lines.

TABLE III

*Computed values of corresponding harmonics for the principal series of sodium.*

Term	$C_0$	$C_1$	$C_2$	$C_3$	$C_4$
1s	$3.38a_0$	$.506a_0$	$.356a_0$	$.217a_0$	$.143a_0$
2p	4.55	....	....	....	....
3p	....	1.28	....	....	....
4p	....	....	1.14	....	....
5p	....	....	....	0.971	....
6p	....	....	....	....	0.830

The values are in terms of  $a_0 = .532 \times 10^{-8}$  cm as unit.

The probability of spontaneous transition  $A'_{,,}$  may now be found from Eq. (2), but as mentioned in Section 2 the representation of  $Q^2\nu_0^4$  as an average of  $C^2\omega_0^4$  may be made in several different ways. Since the



results depend very considerably on the method of averaging the following six methods have been employed:

$$Q^2\nu_0^4 = \frac{1}{2}(C'^2 + C''^2)\nu^4 \quad (A)$$

$$Q^2\nu_0^4 = \frac{1}{4}(C' + C'')^2\nu^4 \quad (B)$$

$$\log Q = \frac{1}{2}(\log C' + \log C'') ; \nu_0 = \nu \quad (C)$$

$$Q^2\nu_0^4 = \frac{1}{2}(C'^2\omega_0'^4 + C''^2\omega_0''^4) \quad (D)$$

$$Q^2\nu_0^4 = \frac{1}{4}(C'\omega_0'^2 + C''\omega_0''^2)^2 \quad (E)$$

$$\log Q\nu_0^2 = \frac{1}{2}(\log C'\omega_0'^2 + \log C''\omega_0''^2) \quad (F)$$

These averages correspond to the six methods of taking a continuous average which have been discussed previously in another connection.<sup>6</sup>

Table IV shows the computed values of  $A'_{ij}$ , as obtained by these six different methods.<sup>12</sup>

TABLE IV

*Relative values of  $A'_{ij}$  for the principal series of sodium.*

Lines	A	B	C	D	E	F
1s-2p	1	1	1	1	1	1
1s-3p	.33	.29	.24	1.2	2.9	.20
1s-4p	.35	.29	.21	4.9	2.8	.16
1s-5p	.33	.24	.15	7.1	3.6	.013
1s-6p	.26	.18	.09	11.0	5.5	.046

TABLE V

*Comparison of computed values of  $A'_{ij}$  with Harrison's measurements.  
Ratios of  $A'_{ij}$  for successive lines*

Lines	A	B	C	F	Experimental
2p/3p	3.0	3.4	4.2	5.0	(4-12)
3p/4p	.94	1.0	1.1	1.3	1.56
4p/5p	1.1	1.2	1.4	2.2	1.38
5p/6p	1.3	1.3	1.7	1.6	1.29

## 5. COMPARISON WITH EXPERIMENT

Relative values of the transition probabilities may be found directly from observed intensities in emission only in the case of two or more lines which have the same initial state. Such sets of lines are of rare occurrence in series spectra as ordinarily observed, and although in a few cases some estimates of intensities for such lines are available it would appear

<sup>12</sup> In a recent paper H. Bartels (Zeits. f. Phys. 32, 415, 1925) has calculated transition probabilities for  $sp$  transitions in sodium, using a method of approximation for the amplitudes similar to that employed by the author. His calculations do not include the principal series transitions, but it is interesting to note that he also comes to the conclusion that averages involving only the stationary states are applicable to  $sp$  transitions, but not to  $pd$  transitions.

that they are too unreliable for a quantitative comparison where so many other uncertainties already enter in.

It may be mentioned here, however, that bolometric measurements of Paschen<sup>13</sup> and Randall<sup>14</sup> on infra-red combination lines of the alkalis give some information as to the relative intensities of certain *sp* and *pd* combinations with the same initial states. These transitions are marked with arrows in Fig. 2. Although probably not very accurate these measurements indicate that the *pd* combinations are in every case more intense than the corresponding *sp* combinations, even though the former correspond to harmonics of lower order than the later. For the reasons given in Section 4 it is not possible to make an estimate by the methods of approximation described here of the transition probabilities for *pd* combinations, but from Fig. 3 we can see that the intermediate states which will be of importance in determining the mean corresponding amplitudes will probably involve large values of the ratio  $\sigma/\omega$ . This fact offers a possible explanation of the abnormally large intensities of the *pd* combinations, as may be seen from Fig. 1 which shows how the amplitudes change with increasing values of  $\sigma/\omega$ . At the same time we must remember that since the statistical weights of initial and final states are not the same for these two types of transition, it may not be possible to compare directly the transition probabilities without taking into account this fact.

The most reliable estimates of transition probabilities at present available seem to be those of Harrison<sup>15</sup> and Slater<sup>16</sup> for the principal series of sodium. These are based on accurate measurements by Harrison of the relative absorption of these lines in sodium vapor, from which the probabilities were deduced by a method devised by Slater. These probabilities may be compared directly with the computed values of Table IV, and Table V shows the ratios of  $A'_{ij}$  for successive lines calculated by different methods of averaging.<sup>17</sup> In the last column are the experimental results of Harrison. The averages D and E have been omitted from Table V as they give values widely at variance with the experimental results. Harrison's measurements give only a rough indication of the values for  $1s-2p$  (the D-lines).

<sup>13</sup> F. Paschen, Ann. der Phys. 33, 717 (1910).

<sup>14</sup> Randall, Ann. der Phys. 33, 739 (1910).

<sup>15</sup> G. R. Harrison, Phys. Rev. 25, 768 (1925).

<sup>16</sup> J. C. Slater, Phys. Rev. 25, 783 (1925).

<sup>17</sup> That the agreement is not as good as indicated in Harrison's paper is due to the fact that the preliminary calculations sent to Dr. Harrison and published by him were found to be in error.

It must be admitted that the agreement by no one of the methods of averaging is very satisfactory. This may be attributed partly to the fact that the method of estimating the corresponding amplitudes is only an approximation, and partly to the fact that if any method of averaging is universally applicable it will certainly not be of a kind which involves only initial and final states.

NATIONAL RESEARCH FELLOWSHIP,  
THE UNIVERSITY OF CHICAGO,  
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## FLUORESCENCE OF CADMIUM VAPOR

BY A. D. POWER

## ABSTRACT

**Fluorescence of cadmium vapor.**—Cadmium vapor, in an evacuated and carefully baked quartz tube, when illuminated by cadmium, iron and nickel sparks, was found to emit the lines 3262A ( $1S-2p_2$ ), 4678A ( $2p_3-1s$ ), 4800A ( $2p_2-1s$ ) and 5086A ( $2p_1-1s$ ) much more strongly from freshly formed vapor than from older vapor. The line 2289A ( $1S-2P$ ) also appeared slightly stronger in the freshly formed vapor when illuminated by the cadmium spark; it was not excited by iron and nickel sparks. Experiments are described which indicate that it was the freshness of the vapor, not primarily the temperature or pressure, which determined the intensity of the radiation. The effective exciting light was absorbed by glass, hence shorter than 3300A. A Cu spark did not excite the lines, at least in the visible.

**Fluorescence of thallium and indium vapors.**—Impurities in the cadmium vapor gave strong fluorescent Th and In lines, ( $2p_2-2s$ ) and ( $2p_1-2s$ ), although spark spectra using the cadmium metal as electrodes did not reveal their presence. These lines were radiated only by the freshly formed vapor and appear to be the result of directly absorbed radiant energy rather than of collisions of the second kind. They were weaker with Cd spark excitation than when light from a Ni or Fe spark was used. Light from a Cu spark excited only the Th lines.

VAN DER LINGEN and Wood<sup>1</sup> have found that mercury vapor under aluminum spark excitation, radiates the line  $\lambda 2537A$  much more strongly when the vapor is freshly formed from the liquid than when the vapor is older. It seemed of interest to investigate the behavior of cadmium vapor under comparable conditions.

In the first experiments, the cadmium was contained in a quartz vessel made from tubing having a diameter of about 3 mm and a length of 7 cm, with a bulb of about 1 cm diameter blown on each end. After introducing the cadmium this vessel was carefully evacuated and sealed off. The exciting spark was focused on one of the bulbs and any desired portion of this bulb was focused upon the slit of a quartz spectrograph, the arrangement being such that a minimum of reflected light entered the latter. The cadmium was maintained at various temperatures and driven from bulb to bulb by suitably arranged Bunsen burners.

It was found that when the cadmium vapor was illuminated by a cadmium spark,  $\lambda 3262A$  with designation  $1S-2p_2$  (accompanied by a bluish-green fluorescence to be discussed later) was emitted much more strongly when the cadmium was evaporating from the bulb than when

<sup>1</sup> Van der Lingen and Wood, *Astrophys. J.* **54**, 149 (1921).

condensing in it. This was expected from the work of van der Lingen and Wood. It was also found that under the same conditions there was a small increase in the intensity of 2289A ( $1S-2P$ ). This increase in intensity of both lines under the same conditions is hardly in accord with the suggestion made by Scott<sup>2</sup> that perhaps at lower vapor pressures mercury entities may be more sensitive to radiation corresponding to 6.7 volts (1849A), while at higher pressures the preference may be for the 4.9 volt (2537A) type. No radiation of the wave-length 1849A ( $1S-2P$ ) is mentioned by van der Lingen and Wood in the work indicated above.

When a nickel spark was used as a source of excitation, the cadmium line 2289A could not be found on any of the plates, but the line 3262A was present, with intensity varying with different conditions in the same manner as when a cadmium spark was used.

Due to the rather narrow bore of the connecting tube there was the possibility of large differences in vapor density, making it impossible to determine whether the variations in intensity of 3262A were due to the age of the vapor or to the variations in density. In order to test this point a new tube was constructed having about 1 cm inside diameter and a length of about 10 cm. The ends were merely rounded off and the tube supported by a quartz rod fused to one end.

In preparing the tube, considerable care was exercised to eliminate gases. It was joined by a constriction to a longer piece of quartz tubing, was heated thoroughly with a glass-blowing burner, and, after the cadmium had been introduced, it was sealed with wax to the vacuum system. The tubing between this seal and the constriction was surrounded by carbon dioxide snow, and a large trap nearer the pumps was cooled in the same manner. A fore-pump and two diffusion pumps in series gave a pressure too low to be measured with a MacLeod gage. Before the final sealing off, all parts of the tube were thoroughly heated several times with the glass-blowing burner, and during this process the cadmium was many times distilled from one part of the tube to another. The final seal was made slowly and at as low temperature as possible.

Experiment showed that the bluish green fluorescence mentioned above could be used as a test for the presence of 3262A and this made the investigation much easier than it otherwise would have been. When the vapor was dense, this fluorescence was confined to the side of the tube where the exciting light entered, but as the pressure was lowered, the fluorescence gradually extended through the whole width of the tube. Three sets of glass-blowing burners having five or six jets each were so arranged that they covered the whole tube except for about an inch at

<sup>2</sup> Scott, *Phys. Rev.* 22, 447 (1923).

the bottom. The temperature of this lower part and thus the pressure, was controlled by three Bunsen burners. With the tube well heated, the liquid cadmium at a red heat and no appreciable condensation of cadmium at any point (a difficult condition to obtain), there was very little if any fluorescence visible even near the cadmium surface. Some fluorescence could exist without detection as there was considerable light due to the burners and spark. Then, without any other changes, one of the Bunsen flames which controlled the temperature of the cadmium was lowered, in order to reduce the vapor pressure. No fluorescence appeared. The temperature was again increased without producing fluorescence. Next some of the flames at the top of the tube were extinguished, and a very brilliant fluorescence appeared at the bottom as condensation occurred at the top. This fluorescence could be obtained for a distance of 4 or 5 cm up the tube, but the intensity fell off rapidly with distance from the cadmium surface.

If the appearance of the visible fluorescence was controlled by vapor density, it should have appeared while the temperature of the liquid cadmium was varied. The removal of the flames from the top of the tube with resulting condensation would cause a large increase in the amount of fresh vapor at the bottom and it was at this time that the brilliant fluorescence appeared. It is believed that this indicates quite definitely that the visible fluorescence and the appearance of 3262A really depend upon the freshness of the vapor, in agreement with the conclusion of van der Lingen and Wood in the case of mercury vapor.

For a general study of the radiations from the tube the glass blowing burners were not needed, one or two Bunsen burners being sufficient. When the vapor was illuminated with the nickel spark, 2289A did not appear, 3262A was very strongly radiated from the fresh vapor, and the visible fluorescence from the fresh vapor was found to contain the first terms of the second subordinate series of triplets 4678A ( $2p_3-1s$ ), 4800A ( $2p_2-1s$ ), and 5086A ( $2p_1-1s$ ). This raises an interesting point. The lower levels occur in the order  $1S$ ,  $2p_{3,2,1}$ ,  $2P$ , and  $1s$ . The lines observed show transfers from  $1s$  to  $2p_{1,2,3}$  and from  $2p_2$  to  $1S$ . Since the transfer from  $1s$  to  $2P$  with wave-length of about 12,800A, is not barred by the selection principle,<sup>3</sup> the transfer from  $2P$  to  $1S$  would be expected; however the corresponding line 2289A did not appear on the plates. It may be that the transfer from  $1s$  to  $2P$  is rare. No record of this line was found in the tables. Whatever the explanation, it appears that the electrons avoided the  $2P$  level under the conditions of the experiment.

<sup>3</sup> Bohr, Ann. der Phys. 71, 228 (1923).

In addition to the above cadmium lines, the fluorescing vapor gave the first pair of the second subordinate series of doublets for both thallium and indium. The lines are 3776A ( $2p_2-2s$ ) and 5350A ( $2p_1-2s$ ) for thallium, and 4102A and 4511A for indium. These metals might be expected as impurities since they occur in the minerals from which cadmium is obtained; the specimen used however, was supposedly quite pure, and spark spectra using the metallic cadmium as electrodes failed to show these impurities. The appearance of their fluorescent spectra under the conditions of the above experiment seems rather surprising since it appears that the concentration of impurities in the vapor state should be even less than in the solid or liquid state.

All the visible fluorescence disappeared when a sheet of glass was interposed between the spark and the quartz tube, showing that the radiations originated in the vapor and were produced by a wave-length shorter than 3300A.

No means were readily available for isolating the various ultraviolet lines of the exciting radiation, and so little can be said about the energy changes accompanying the radiations from the vapor. The thallium and indium vapors may have absorbed radiation directly from the spark, or may have received their energy through collisions of the second kind as studied by Franck and his students. The first explanation seems to be the more probable because while nickel and iron sparks brought out strongly all the lines mentioned above, the cadmium spark did not bring out the thallium and indium lines strongly, although the cadmium lines appeared with full intensity. The cadmium spark should have brought out the thallium and indium lines if they depended upon collisions of the second kind.

The results of nickel, iron and cadmium spark excitation have been indicated. Aluminum, tin, and lead sparks produced feeble fluorescence. Copper brought out the thallium line 5350A quite well but not the other visible lines.

Van der Lingen<sup>4</sup> while studying the absorption by cadmium vapor of the radiations from a cadmium spark, found no trace of visible fluorescence. It seems probable that he confined his work to lower temperatures than those used in the present work, and this may be the explanation.

The writer desires to express his obligation to Professor J. T. Tate for suggestions, criticism and interest during the progress of the work.

UNIVERSITY OF MINNESOTA,

MINNEAPOLIS, MINN.

August 3, 1925.

<sup>4</sup> Van der Lingen, *Zeits. f. Physik* 6, 403 (1921).



THE ABSORPTION SPECTRUM OF MANGANESE VAPOR  
IN THE VISIBLE AND ULTRAVIOLET

By R. V. ZUMSTEIN

## ABSTRACT

With an absorbing column of the vapor about 3 cm long heated to temperatures between 1200°C and 1600°C, absorption was observed at 31 lines. Grotrian had previously reported absorption at 6 of these lines. All of the absorptions are from manganese atoms in the normal state ( $1^6s$  term) and occur in groups of 1, 2 and 3 lines. Five absorption lines represent  $1^6s-d'$  combinations for which the rule of inner quantum numbers is obeyed but the azimuthal quantum number changes by 2. Four lines are  $1^6s-8p$  combinations and twelve are  $1^6s-6p$  combinations. Some of the remainder are perhaps  $1^6s-4p$  and  $1^6s-2p$  combinations.

THE spectrum of manganese is of particular interest as the article by M. A. Catalan<sup>1</sup> on the series spectrum of that element was the starting point of the theory of multiplets. The absorption spectrum of the vapor has been studied by Grotrian<sup>2</sup> who observed absorption at 6 lines. The present experiments were undertaken with the same method that has been employed for copper, silver, gold and lead<sup>3</sup> but with some important improvements. The spectrum from 6000 to 3800Å is photographed with a 2 prism glass spectroscope, from 4000 to 2170Å with a large Hilger quartz instrument size E<sub>1</sub>, from 2170 to 1950Å with a quartz spectroscope made in the Physics Shop of the University of Michigan and having slightly greater dispersion than the Hilger size E<sub>2</sub>.

An ordinary 100 watt tungsten lamp was used as source of light for the visible spectrum. Below 4000Å, a 75 ampere lead arc was employed. The upper terminal was a 1 cm carbon rod and the lower terminal a pool of molten lead 2 cm in diameter. The distance between the terminals was about 5 mm. This arc gives an intense continuous radiation from the visible to 1850Å, with the more intense lead arc lines reversed. The intensity of the continuous radiation is so great that the manganese absorption lines at 2000Å could be photographed in less than 1 minute. The vapor was obtained as before by heating the manganese in a small carbon tube with an oxy-acetylene torch to about 1600°C.

<sup>1</sup> M. A. Catalan, *Trans. Roy. Soc.* **223**, 127 (1922).

<sup>2</sup> W. Grotrian, *Zeits. f. Phys.* **18**, 169 (1923).

<sup>3</sup> Zumstein, *Phys. Rev.* **25**, 523 and **26**, 189 (1925).

<sup>4</sup> H. N. Russell, *Astrophys. J.* (May 1925).

Table I gives the wave-lengths at which absorption was observed. The intensities are those of the absorption lines on the basis of  $I=10$  for the strongest lines, and are only rough estimates. The interpretation of the present experiments is based on Catalan's article, the energy diagram of manganese given in Sommerfeld's *Atombau* etc. 4th Ed., p. 702 and the scheme of the inner quantum numbers on page 591 of the same book.

Faint absorption was observed corresponding to the two emission lines 5394 and 5432. These were designated by Catalan as the inter combination lines  $1S-1p_2$ ,  $1S-1p_3$ . Following H. N. Russell<sup>4</sup> we will call them

TABLE I  
*Manganese absorption lines observed*

$\lambda$ (I.A.)	Int.	$\nu$ (I. vac.)	$\lambda$ (I.A.)	Int.	$\nu$ (I. vac.)
5394.070	1	18531.65	2208.73	8	45260.8
5432.555	1	18402.45	2184.84	1	45755.5
4034.489*	6	24779.31	2174.09	1	45981.6
4033.074*	6	24788.01	2173.16	1	46001.3
4030.760*	6	24802.23	2109.55	5	47388.4
3224.769	2	31001.10	2106.03	5	47467.6
3216.954	2	31076.36	2097.48	3	47661.1
2801.076*	10	35690.07	2093.29	5	47756.4
2798.273*	10	35725.82	2092.33	5	47778.3
2794.822*	10	35769.94	2091.93	5	47787.4
2384.04	2	41932.6	2072.6	1	48232
2377.12	2	42054.7	2071.1	1	48283
2372.12	2	42143.4			
2296.86	3	43524.2	2003.4	9	49900
2221.80	9	44994.6	1998.4	9	50022
2213.80	9	45157.1	1995.1	9	50108

\* Reported by W. Grottrian

$1^6s-1^8p$  combinations, thereby indicating that they are combinations between the  $1s$  term of the sextet system and the  $1p$  term of the octet system. The normal state of the manganese atom corresponds to a  $1^6s$  term. This pair of lines can be excited with the least energy of all the lines of the manganese spectrum. The fact that their intensity in the arc and absorption spectrum is weak is in agreement with the rule that inter combinations between two systems (here sextet with octet) are weak while combinations in the same system (sextet with sextet) would give strong lines. The absorption observed at this pair is perhaps the best evidence afforded by the present experiments that the energy diagram as given by Sommerfeld is correct.

The narrow triplet 4030, 4033 and 4034 is easily reversed in the arc and also strongly absorbed by the vapor. They are  $1^6s-1^6p$  combinations

<sup>4</sup> Catalan, Anal. Soc. Esp. Fis. y Chim. 21, 321 (1923).

and were previously observed by Grottrian as absorption lines of the vapor. At higher temperatures these lines broaden and appear as one strong absorption line.

Two sharp absorption lines which showed no broadening with increase of temperature were observed at 3224.769 and 3216.954. Being a doublet, the scheme for the inner quantum numbers would suggest that they are  $1^6s-^8p$  or  $1^6s-^4p$  combinations. If we suppose at first that they are  $1^6s-^8p$  combinations then they define two  $^8p$  terms which would combine with the  $2^8s$  term (9779.89) to give two emission lines 5239.32 and 5218.73. Similarly with the  $2^8d$  term (13224 etc.) we would get 6395.37 and 6364.76. The fact that these four predicted lines are not given as manganese lines makes it probable that this doublet represents a  $1^6s-^4p$  combination. Unfortunately one cannot test this point as no combinations between the quartet system and the other two are known. Several multiplets of the quartet system were given by Catalan<sup>5</sup> and by Back<sup>6</sup> but the observed frequency difference 75.26 is not given by them.

The triplet 2794, 2798, 2801 is a  $1^6s-2^6p$  combination and was previously observed in absorption by Grottrian. At higher temperatures (about 1600°C) the triplet appears as one broad absorption line.

The triplet 2384.04, 2377.12, 2372.12 was always observed as sharp narrow lines in absorption, of the same appearance as reversals in the arc. It is a  $1^6s-1^6d'$  combination involving the  $d'$  level defined by multiplet 6 of Catalan. Lines 2384.04 and 2372.12 were given by Fuchs<sup>7</sup> as manganese arc lines; 2377.12 was not given by Fuchs and is my own measurement. For this group, the rule for inner quantum numbers is obeyed but the azimuthal quantum number changes by 2 units. Similar transitions have been reported by other experimenters.

The triplet 2221.80, 2213.80 and 2208.73 is a  $1^6s-3^6p$  combination with the  $p$  terms defined by multiplet 5. They showed considerable broadening when reversed in the arc and when absorbed by the vapor. In this region of the spectrum, the iron and manganese arcs were photographed for comparison. This triplet appeared as strong reversed lines in the manganese arc and as strong emission lines in the iron arc. The values here given for their wave-lengths are taken from Schuhmacher's<sup>8</sup> table of the iron lines. No connection with the series scheme could be found for the absorption lines 2296.86 and 2184.84. Their appearance as single isolated lines would indicate that they may be  $1^6s-2^6p$  combinations.

<sup>5</sup> E. Back, *Zeits. f. Phys.* 15, 206 (1923).

<sup>7</sup> H. Fuchs, *Zeits. f. Wiss. Phot.* 14, 279 (1915).

<sup>8</sup> Kayser and Konen, *Spektroskopie* 7, p. 486.

The  $2^8p$  term (13956.1) given by Catalan as doubtful should of course be a 3 fold term and should combine with the normal  $1^6s$  term (59937.47) to give a doublet in absorption. The frequency of one of these absorption lines would be  $59937.47 - 13956.1 = 45981.4$ . A faint absorption line was observed on several plates of frequency 45981.6. This line was also reversed in the manganese arc. Nearby and apparently forming a doublet with this line is one of frequency 46001.3 which was of the same intensity and found to be reversed in the arc and absorbed by the vapor. If this doublet represents a  $1^6s-2^8p$  combination, then we should expect a strong infrared line of frequency greater than that of  $\lambda 15263.8$  by 19.7. Randall and Barker<sup>9</sup> give a line of intensity 80 and differing in frequency from  $\lambda 15263.8$  by 17.9. This is therefore very good evidence that two members of the  $2^8p$  term are 13956.1 and 13937, the third member being still unknown.

There is a group of 6 manganese absorption lines between 2109 and 2091A which are of especial interest. They are so strongly absorbed by the vapor that I expected no difficulty in fitting them in the series scheme. These expectations were far from fulfilled. 2097.48 was reversed in the arc spectrum and absorbed by the vapor as a sharp absorption line even at the highest temperatures ( $1600^\circ$ ). No combination lines between the term defined by this line and the other known manganese terms were observed. The other five lines of the group showed considerable broadening at high temperature, the two lines 2092.33 and 2091.93 appearing as one absorption line. From the magnitude of the absorption it was fairly certain that these lines represented combinations between the  $1^6s$  term and  $p$  terms of the same system ( $^6p$  terms). These  $^6p$  terms should combine with the  $1^6d$  term to give a group of lines between 3400A and 3200A. The spectrum of a manganese arc of 125 amperes was therefore photographed with a quartz spectroscope having a dispersion of 7A per mm and examined for reversals, it having been previously noted that an arc of this magnitude gave as reversals all multiplets from the  $1^6d$  term and from the  $1^8p$  term. In this region of the spectrum 24 lines were observed reversed in addition to multiplet 9. These lines are all given in Fuchs' list with the exception of 3339.5. However the dispersion of the spectroscope was not great enough to be certain of the results in some cases.

$\lambda 2109.55$  defines a  $p$  term (12549.1) which combines with the  $1^6d$  terms having inner quantum numbers  $7/2$  and  $5/2$ . For the  $p$  term  $j$  (inner quantum number) is therefore  $7/2$  or  $5/2$ .  $\lambda 2106.03$  defines a

<sup>9</sup> Randall and Barker, *Astrophys. J.* 49, 59 (1919).

$p$  term (12469.9) which combines with the  $1^6d$  terms for which  $j$  is  $1/2$ ,  $3/2$  and  $5/2$ . The value of  $j$  for this term is  $3/2$ .  $\lambda 2093.29$  defines a  $p$  term (12181.1) which combines with the  $1^6d$  terms of inner quantum numbers  $3/2$  and  $7/2$ . For the  $p$  term  $j$  is  $5/2$  (?). The absence of the  $5/2$  combination makes this uncertain.  $\lambda 2092.33$  defines a  $p$  term (12159.2) which combines with  $1^6d$  terms ( $j=9/2, 7/2, 5/2$ ). For the  $p$  term  $j$  is  $7/2$ .  $\lambda 2091.93$  defines a  $p$  term (12150.1) which combines with  $1^6d$  terms ( $j=1/2, 3/2, 5/2$ ). The  $j$  value of the  $p$  term is  $3/2$ . For these last two  $p$  terms the agreement between the observed and calculated frequencies is not very good. This is probably connected with the difficulty of getting accurate measurements of the wave-lengths of

TABLE II

*New combinations with the term  $1^6d$  (17052.30)*

$p$ term	$j$	$\nu$ calc	$\nu$ observed as reversal	$\lambda$ observed
12549.1	( $7/2$ or $5/2$ )	29936.9 30106.4	29936. 30105.62	3339.5 A 3320.698
12469.9	$3/2$	29830.6 29899.2 30016.1	29829.50 29898.18 30015.34	3351.427 3343.728 3330.676
12181.1	$5/2?$	30188.0 30474.4	30185.26 30472.15	3311.925 3280.744
12159.2	$7/2$	30326.8 30496.3 30726.0	30322.97 30492.49 30722.19	3296.884 3278.553 3254.040
12150.1	$3/2$	30150.4 30219.0 30335.9	30145.32 30213.83 30330.83	3316.324 3308.791 3296.029

the two absorption lines. In Table II are collected these five  $p$  terms, the values of  $j$  as I have assigned them, the frequencies calculated for the combination of the  $p$  term with certain members of the  $1^6d$  term, also the frequency of a reversed line on my plates, and finally the wave-length of this reversed line. Three of the  $p$  terms may be calculated directly from the arrangement given by Catalan (page 157) for a group of 10 lines which is obviously a mixture of several multiplets.

A second  $^6d'$  term is fixed by multiplet 9 and we should expect the combination between this term and  $1^6s$  to appear as a narrow triplet in absorption. Two of the predicted lines were readily observed as such on several plates  $\lambda 2072.6$  and  $\lambda 2070.4$ . The third member if present was of much less intensity than the two observed.

Finally we have the triplet 2003.4, 1998.4, 1995.1A. All of these lines were strongly reversed in the arc and as absorption lines had considerable width. They are  $1^6s-4^6p$  combinations with the  $4^6p$  term defined by multiplet 7.

It is worth noting that no absorptions were observed that would indicate atoms in the  $1^8p$  or  $1^6d$  state. The frequency difference between the normal state and  $1^6d$  is 17052.3. The temperature of the vapor was apparently not sufficient to put the atoms in these excited states. In conclusion we may say that the absorption spectrum of manganese contains a relatively small number of intense lines and that they occur in groups of 1, 2 or 3 lines. This is exactly what one would expect if the normal state of the atom corresponded to an  $s$  term.

NATIONAL RESEARCH FELLOWSHIP,  
PHYSICS DEPARTMENT,  
UNIVERSITY OF MICHIGAN,  
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CHANGE IN THE INFRA-RED ABSORPTION SPECTRUM  
OF WATER WITH TEMPERATURE

J. R. COLLINS

## ABSTRACT

By the use of two constant deviation spectrometers in series and a Coblentz linear thermopile, the absorption coefficient of water was measured for various temperatures from 0° to 95°C. The bands found showed maximum absorption at the following wave-lengths

at 0°C:	.775	....	.985	1.21	1.45	1.96 $\mu$
at 95°C:	.74	.845	.97	1.17	1.43	1.94 $\mu$

There is a shift toward shorter wave-lengths as the temperature increases and also a marked increase in magnitude of the maximum absorption for the bands at .77, .98 and 1.21 $\mu$ . These changes are qualitatively explained by Roentgen's hypothesis that water is a mixture of at least two kinds of molecules, presumably (H<sub>2</sub>O)<sub>2</sub> and (H<sub>2</sub>O)<sub>3</sub>, whose relative amounts change with a change of temperature.

## INTRODUCTION

BEGINNING with Roentgen<sup>1</sup> in 1892, the anomalous properties of liquid water have been explained by assuming that it is composed of two or more kinds of molecules. Roentgen assumed that there were two, which he termed water molecules and ice molecules. They are now generally called dihydrol and trihydrol on the supposition that they are the double and the triple molecule of water. Sutherland<sup>2</sup> has calculated the relative proportions of these constituents at various temperatures from the density-temperature curve by making certain assumptions about the densities of the constituents. Later writers<sup>3</sup> have made it seem likely that liquid water is composed of three components, namely, the simple, the double, and the triple molecule. The amount of hydrol, the simple molecule, at the freezing point is extremely small, and the amount of trihydrol at temperatures much above the normal boiling point is not great. The amount of hydrol and dihydrol increases at the expense of the trihydrol as the temperature increases from the freezing point, and at higher temperatures, presumably above the normal boiling point, the amount of dihydrol begins to decrease.

The relative amounts of the different constituents of liquid water may be changed by changing the physical conditions of the water, such as the

<sup>1</sup> Roentgen, Wied. Ann. 45, p. 91 (1892).

<sup>2</sup> Sutherland, Phil. Mag. 50, p. 460 (1900).

<sup>3</sup> Bousefield and Lowry; Guye, Proc. Faraday Soc. 6, p. 85 (1910).



temperature, pressure, by the addition of dissolved substances, etc. Hudson<sup>4</sup> has shown, that, in the absence of hydration, the presence of dissolved substances results in a decrease in the amount of trihydrol. The change in the infra-red absorption spectrum of liquid water due to the presence of dissolved substances has been studied by several investigators.<sup>5</sup> It was suggested by the present author<sup>6</sup> that this change was due to the change in the relative proportions of two or more kinds of molecules present in the water. The formation of hydrates by the dissolved substance complicates the results, of course, and makes the interpretation of the absorption curves more difficult.

The absorption spectrum of liquid water should change with an increase in temperature in the same way as it changes as a result of the addition of a dissolved substance. The present paper gives the results of measurements of the absorption of liquid water at various temperatures between 0° and 100°C and throughout the spectral range from 0.7 to 2.1 $\mu$ .

#### APPARATUS AND EXPERIMENTAL PROCEDURE

The apparatus for determining the absorption of water is the same as that used by the author in a previous investigation.<sup>6</sup> Two constant deviation spectrometers were used in series to eliminate stray radiation, and a Coblentz linear thermopile was placed at the exit slit of the second spectrometer to measure the intensity of the radiation falling on it. The cell containing the water was held on a slider so that it could be placed in the beam of radiation passing through the spectrometers. The source of radiation was a 6000 lumen series street lighting incandescent lamp.

Inasmuch as the positions of some of the absorption bands of water determined by this apparatus did not agree with the results of other workers, the calibration of the spectrometer was carefully repeated. In addition to the emission lines of certain metals used previously, a film of air 0.000736 cm in thickness was placed in front of the slit of the spectrometer and the transmission of this film determined throughout the spectral range to be used for the study of water. The positions of the interference bands throughout the spectrum were calculated by use of observations made in the visible spectrum. Good agreement was obtained by the two methods, and good agreement with the previous calibration except in the region near 2.0 $\mu$ . In this region the emission lines were rather faint

<sup>4</sup> Hudson, *Phys. Rev.* 21, p. 16 (1905).

<sup>5</sup> H. C. Jones et al., *Phys. Zeits.* 14, p. 278 (1913); 15, p. 447 (1914);

Angstrom, *Phys. Rev.* 3, p. 47 (1914);

Grantham, *Phys. Rev.* 18, p. 339 (1921).

<sup>6</sup> Collins, *Phys. Rev.* 20, p. 486 (1922).

and difficult to locate accurately. The interference method was much more satisfactory in this region and the results from that method were used.

A double-walled brass cylinder was constructed to hold the absorption cell, and either ice or an electrical heating coil was placed around the inner cylinder to maintain the cell at constant temperature. Various thicknesses of water were used for the different portions of the spectral range covered by the experiments. The thicknesses used were: 10 cm from 0.70 to 0.90 $\mu$ ; 2 cm from 0.90 to 1.10 $\mu$ ; 1 cm from 1.10 to 1.30 $\mu$ ; 0.04 cm from 1.30 to 1.70 $\mu$ ; 0.0076 cm from 1.70 to 2.10 $\mu$ . The temperature of the water was determined by a thermocouple of copper and advance. In the case of the thicker layers the junction of the couple was in the water, while in the case of the two thinner layers the junction was in contact with the glass end of the cell containing the water. The distilled water used was boiled before using and no trouble was encountered due to bubbles in the cell.

In the case of the three thicker cells, a thinner cell was used for comparison to eliminate the effect of reflection at the surfaces. Except for room temperature, no comparison cell was used in the case of the two thinner cells. For other temperatures the reflection was calculated by means of Fresnel's formula. The lack of accurate correction for reflection does not lead to serious error, as the important thing here is the comparison of the absorption at different temperatures, which is unaffected by the reflection correction.

The experimental procedure was to hold the water at a constant temperature and to determine the transmission of the water throughout the spectral range for which the particular thickness of water was suitable. The thermopile was connected to a Leeds and Northrup high voltage sensitivity galvanometer for which a telescope and scale were provided. The scale was about five meters distant, and for the deflections used (up to 150 divisions) the readings were proportional to the voltage; hence they were taken as proportional to the intensity of radiation falling on the thermopile. After such a series of readings, the temperatures of the cell was changed to another constant value and transmission data taken for that temperature. For some positions in the spectrum, data were taken with the spectrometer setting constant and the temperature of the water changed to various values. This procedure is of particular value on the steep slope of an absorption band.

## EXPERIMENTAL RESULTS

Figs. 1 to 6 show the results obtained for the six absorption bands of water studied. The mass coefficient of absorption is plotted as a function of the wave-length. The mass coefficient

$$k = (1/t\rho) \log (d_0/d)$$

is used because it is a quantity comparable at various temperatures. In this expression  $t$  is the thickness of the water layer,  $\rho$  is the density of the water at the temperature for which  $d$  is the galvanometer deflection when the cell is in the path of the radiation, and  $d_0$  is the galvanometer deflection when nothing is in the path of the radiation. The slit width

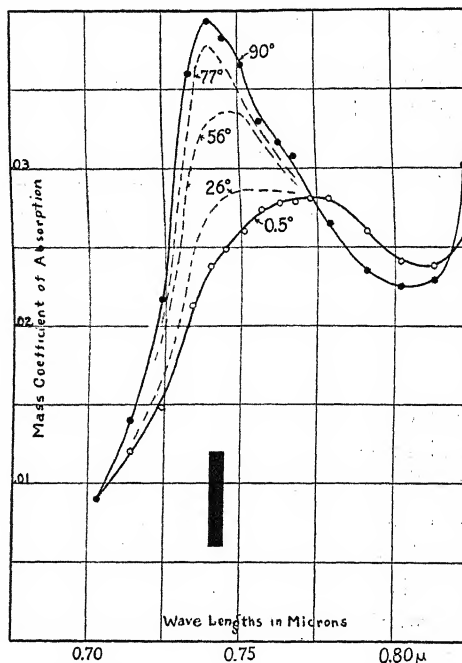


Fig. 1. Absorption band (.70—.80 $\mu$ ) of liquid water at 0.5° to 90°C.

is indicated by a black strip below the curves. Complete curves are given for the highest and lowest temperatures, while for the intermediate temperatures a portion only of each curve is plotted to avoid confusion. In all portions of the spectrum the values of the coefficient for the intermediate temperatures fall in the order of the temperatures.

In all of the absorption bands, an increase in the temperature resulted in a shift of the position of the maximum absorption toward shorter wave-lengths. Probably the most striking change in a band is shown in

Fig. 2 ( $0.85\mu$ ). At low temperatures there is just a faint indication that a band is in this region, but with increasing temperatures the band becomes very pronounced. Except in Fig. 5 an increase in temperature produces an increase in the value of the maximum coefficient. The results in Fig. 4 are probably not very accurate on account of the fact that the width of the slit is comparable to that of the band.

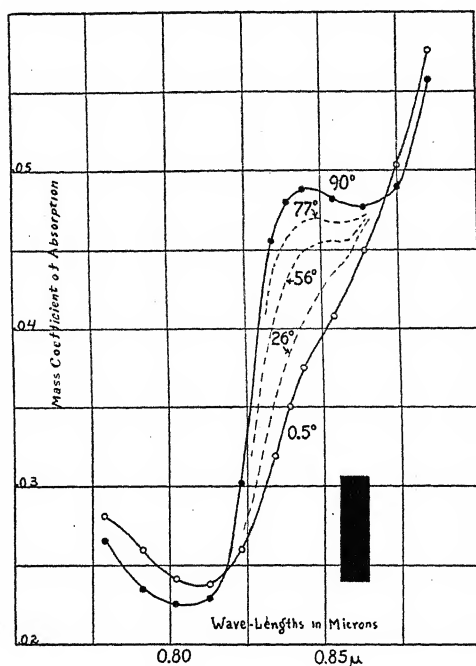


Fig. 2. Absorption band ( $0.8-0.9\mu$ ) of liquid water at  $0.5^{\circ}$  to  $90^{\circ}\text{C}$ .

The positions of the maximum coefficient for the various absorption bands and the values of the maximum coefficients are given in Table I.

TABLE I

*Effect of change of temperature on the absorption bands of water*

Wave-length of max. absorption		Shift	Max. mass coeff. of absorption	
$0^{\circ}\text{C}$	$95^{\circ}\text{C}$		$0^{\circ}\text{C}$	$95^{\circ}\text{C}$
0.775 $\mu$	0.740 $\mu$	.035 $\mu$	0.0280	0.0395
0.845	0.845	0	0.430	0.0490
0.985	0.970	.015	0.430	0.630
1.21	1.17	.04	1.28	1.43
1.45	1.43	.02	29.8	29.8
1.96	1.94	.02	108	112

The values of the maximum absorption coefficients are in good agreement with those of Jones<sup>5</sup> and with those of Dreish.<sup>7</sup> The values given

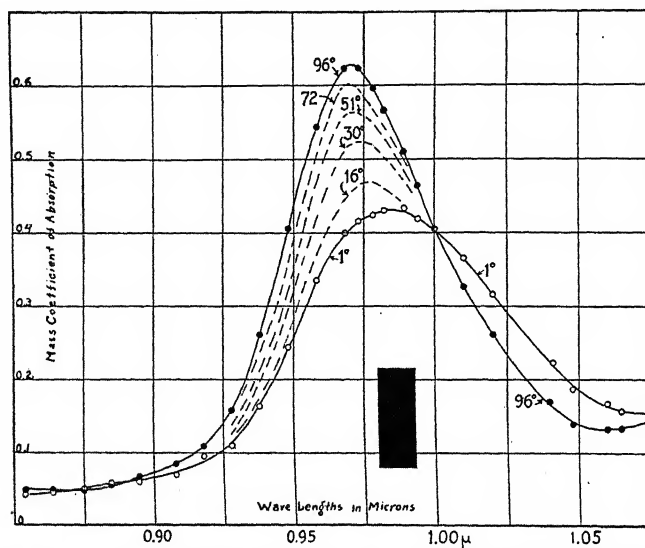


Fig. 3. Absorption band (0.9–1.05 $\mu$ ) of liquid water at 0.5° to 90°C.

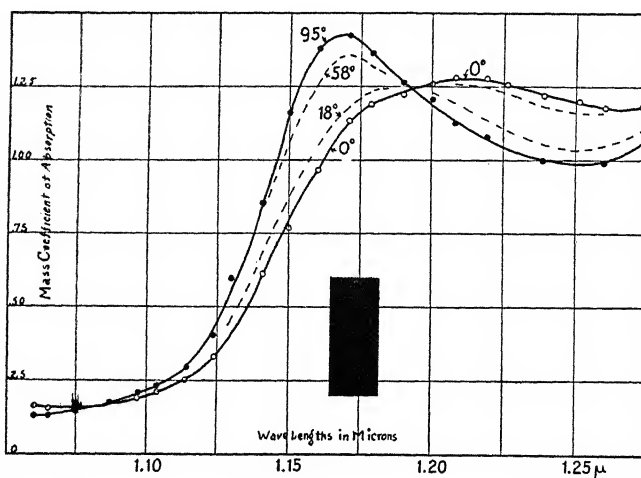


Fig. 4. Absorption band (1.1–1.25 $\mu$ ) of liquid water at 0.5° to 90°C.

by Aschkinass<sup>8</sup> for the bands at 1.46 and 1.96 $\mu$  are much higher than those of Dreisch and in the present paper. The difference is probably due to an error in his thickness measurements.

<sup>7</sup> Dreish, *Zeits. f. Physik* 30, p. 200 (1924).

<sup>8</sup> Aschkinass, *Ann. d. Physik* 55, p. 401 (1895).

## DISCUSSION OF RESULTS

The explanation offered to account for the change in the absorption of liquid water is that indicated in the first part of the paper. We may assume that there are two kinds of molecules present in the water,

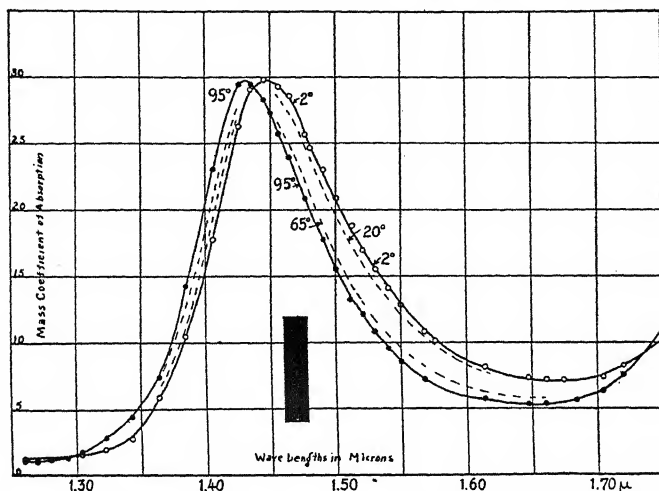


Fig. 5. Absorption band ( $1.3-1.7\mu$ ) of liquid water at  $0.5^\circ$  to  $90^\circ\text{C}$ .

neglecting the effect of change in the amount of hydrol. The absorption spectrum of dihydrol is assumed to have its bands at slightly shorter wave-lengths than does that of trihydrol. The comparison of the ab-

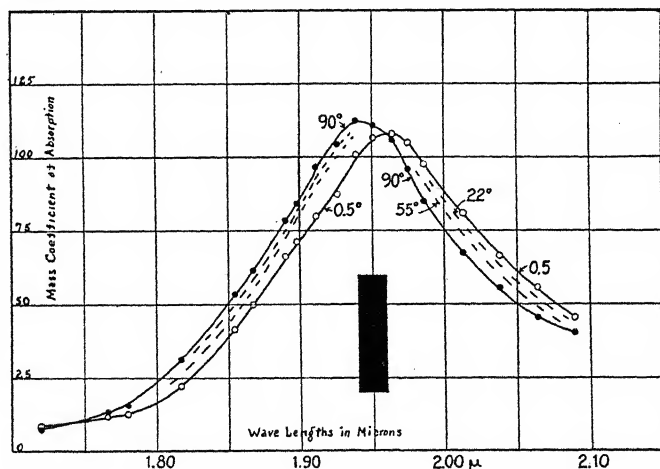


Fig. 6. Absorption band ( $1.8-2.1\mu$ ) of liquid water at  $0.5^\circ$  to  $90^\circ\text{C}$ .

sorption spectra of water vapor, liquid water, and ice indicates that the bands of dihydrol near  $1.45$  and  $1.96\mu$  are not so intense as the cor-

responding bands of trihydrol. The other bands at shorter wave-lengths are more intense for dihydrol. In Fig. 7, the mass coefficient of absorption of water vapor, as given by Hettner<sup>9</sup> and by Dreisch,<sup>7</sup> and of liquid water, as given by Dreisch and in the present paper are plotted; the position of the ice absorption bands, as given by Plyler,<sup>10</sup> are also indicated. It is seen that there are corresponding bands in all the modifications of water. As the molecular structure gets more complex, the positions of maximum absorption shift towards longer wave-lengths. In the absorption bands near  $1.45$  and  $1.96\mu$  the intensity of the bands increases with increasing complexity of the molecule, while in the bands at shorter wave-lengths the reverse is true.

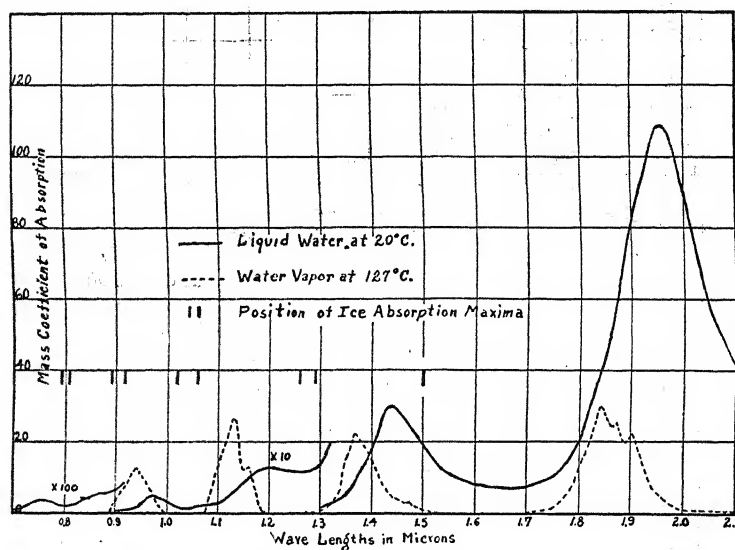


Fig. 7. Comparison of the absorption bands of liquid water with those of water-vapor and of ice.

If the observed absorption spectrum of liquid water is the result of superposing the absorption spectra of dihydrol and trihydrol, the result would be, if the corresponding bands are very close together, a broader band than either component would have alone. As the temperature increases, the intensity of the dihydrol bands increases, while that of the trihydrol decreases. This would produce an apparent shift in the position of the maximum absorption in the observed band toward the shorter wave-lengths. For the absorption bands in which the intensity is greater for the dihydrol than for the trihydrol, the result of increasing tempera-

<sup>9</sup> Hettner, *Ann. d. Physik*, **55**, p. 476 (1919).

<sup>10</sup> Plyler, *J. Opt. Soc. Amer. and R.S.I.* **9**, p. 545 (1924).



ture would be an increase in the intensity of the observed band. Both of these changes are observed to occur. In the cases where the intensity of the absorption is greater for the trihydrol, it is less certain what should happen to the intensity of the observed band. The number of dihydrol molecules resulting from the splitting up of the trihydrol is one and a half times the number of the trihydrol molecules, so that in spite of the decrease in the coefficient of absorption, the actual absorption of the dihydrol might be as great or greater than that of the trihydrol. This is apparently what has happened in the bands at  $1.45$  and  $1.96\mu$ .

In all the bands, except that at  $1.96\mu$ , it will be observed that there is a decided narrowing, as would be expected if the amount of trihydrol present at the higher temperatures is small compared to the amount of dihydrol. According to Guye<sup>3</sup> this is the case, although there seems no method at present to determine the relative proportions of the constituents accurately enough for any quantitative check.

CORNELL UNIVERSITY,

August 25, 1925.

THE CRITICAL POTENTIAL OF THE NEGATIVE  
BAND SPECTRUM OF NITROGEN

ENOS E. WITMER\*

## ABSTRACT

The method used was to photograph the spectrum of the light excited inside an equipotential anode by electrons from a filament distant less than an electron mean free path. The straight filament of tungsten was placed 2 mm in front of the anode, a nickel pill box which was perforated with numerous holes on the side facing the filament. A rectangular opening in the convex side of the box permitted spectroscopic observation of the glow developed within. Chemically prepared nitrogen at about 0.1 mm pressure was used and precautions taken to ensure its purity. Using a Hilger constant deviation glass spectrograph, a series of spectrograms was obtained in the region above  $\lambda 3900\text{\AA}$  at intervals of a volt from 17.75 to 22.75 volts (corrected) inclusive. The negative bands which are fairly intense at 22.75 volts gradually decrease in intensity as the voltage decreases, but on the 17.75 volt spectrogram 4278 is distinctly visible and there are traces of 4708 and 4236. These results seem to indicate that the negative bands appear as a whole at the ionization potential of nitrogen or between the ionization potential and 17.75 volts.

SINCE the method of electron impact has played such an important role in the study of line spectra and atomic structure, it is natural to suppose that it will prove of great importance in the study of band spectra and molecular structure. Up to the present, however, very little work has been done in this field. It is true that critical potentials have been determined for a number of substances in the molecular state, but the relation between these critical potentials and the spectrum emitted by the molecule has been investigated in only a few instances.

Nitrogen has a number of band groups. Kayser in his "Handbuch der Spektroskopie" mentions seven which have been ascribed to it. The identity of the molecule emitting several of these groups is in doubt, however. Three of the most important groups are the first and second positive groups, which lie in the visible and infrared, and the negative group, which lies in the visible and ultraviolet.

Bloch and Bloch<sup>1</sup> photographed the spectrum of nitrogen in the presence of mercury vapor at various voltages and came to the conclusion that the second positive spectrum appears at about 10 or 12 volts and the negative band  $\lambda 3914$  at 21.5 volts. These critical potentials do not seem to coincide with any of the resonance and ionization

\* Harrison Research Fellow, University of Pennsylvania.

<sup>1</sup> Bloch and Bloch, *Comptes Rendus* 170, 1380 (1920); 173, 225 (1921).

potentials reported by various investigators. Using the photo-electric method of detecting radiation, Brandt<sup>2</sup> found a series of critical potentials between 7.5 and 8.2 volts. The spectral frequencies corresponding to these critical potentials (as determined by the relation  $h\nu = W_1 - W_2$ ) suggested by their distribution a series of band heads. Foote, Mohler, and Meggers<sup>3</sup> investigated the spectrum of nitrogen in the presence of sodium vapor and found that the positive bands appear at 7 volts and that the negative band group is intense at 25 volts. Duffendack and Duncan<sup>4</sup> found that the first and second positive bands appear below the ionization potential and the negative bands above the ionization potential. The former they ascribed to the neutral molecule and the latter to the ionized molecule. More recently Duffendack<sup>5</sup> has come to the conclusion that the critical potential for the negative bands is 18.5 volts. The apparent discrepancies in these results show that further investigation of nitrogen is necessary.

In the present investigation the spectrum of the nitrogen glow in a two element electron tube was photographed at various plate voltages by the use of a Hilger constant deviation spectrograph with glass prisms and lenses. The investigation was limited to the region above  $\lambda 3900$ .

#### DESCRIPTION OF APPARATUS

The experimental tube shown diagrammatically in Fig. 1 was of Pyrex glass, 3.8 cm in diameter. The cathode *F* was a straight filament of tungsten, 15 mils (.38 mm) in diameter. A thick filament was used in order to keep the potential drop in it as small as possible. The filament could be replaced by removing the stopper *S*, which was made of 702P glass. The stopper was accurately fitted to the main part of the tube by a ground joint. Because of the large amount of heat developed in the filament it was necessary to use water-cooling. This was provided by a water chamber *w* in the stopper, with inlet and outlet tubes *EE*, through which water circulated. The portion of the filament leads at *A* and *B* where they pass through the glass were of tungsten. The filament was held in place by bushings provided with screws as shown in the figure. The anode consisted of a nickel pill box *N* which was perforated with numerous holes in the side facing the filament, so as to form a grid. A rectangular opening in the side of the box permitted spectroscopic observation of the interior. The filament was placed 2 mm from the

<sup>2</sup> Brandt, *Zeits. f. Phys.* **8**, 32 (1921).

<sup>3</sup> Foote and Mohler, *Origin of Spectra*, p. 190.

<sup>4</sup> Duffendack and Duncan, *Phys. Rev.* **23**, 295 (1924).

<sup>5</sup> Duffendack, *Astrophys. Jour.* **61**, 209 (1925).

perforated face of the anode. The anode lead was sealed in at *G* with sealing wax, as were the filament leads at *C* and *D*. The nickel box used as anode was covered both inside and outside with a film of lampblack to prevent the scattering of the light of the filament.

This two element tube was connected through a liquid air trap, a stopcock, and another liquid air trap to the pumps, a McLeod gauge, a bulb of phosphoric anhydride, and a nitrogen reservoir. The pumping system consisted of two mercury diffusion pumps connected in series, and an oil backing pump.

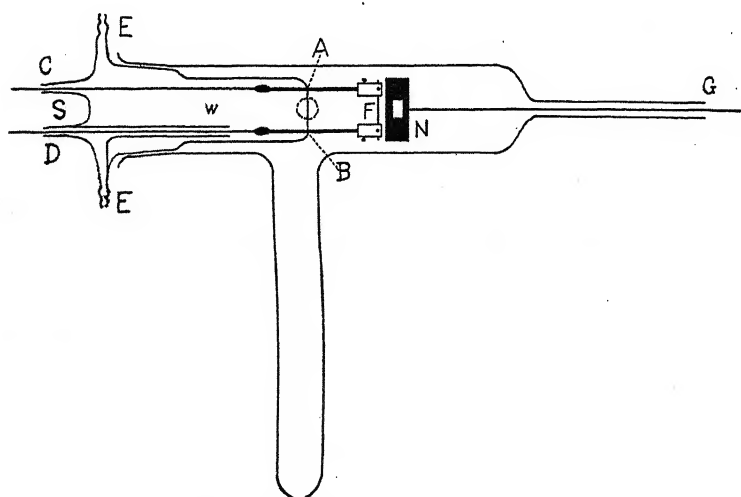


Fig. 1. Discharge tube showing pill box *N* in which glow is produced by electrons from filament *F*.

The filament required from 14 to 18 amp. The current for heating it was obtained from a 110 volt d.c. generator. The plate potential was obtained from a potential divider connected to a storage battery. The negative side of the plate potential was connected to the negative side of the filament.

Wratten and Wainwright Panchromatic Plates were used for photographing the spectrum.

#### EXPERIMENTAL PROCEDURE

In the final experiments chemically prepared nitrogen was used. This was made by the reaction of ammonium sulfate, sodium nitrite, and potassium dichlorate. The gas evolved was passed through water, a solution of sodium hydroxide, and finally liquid air traps for purification. The color of the glow obtained seemed to afford an index of the purity

of the nitrogen. The nitrogen glow is pink at low voltages, but certain impurities change this color to blue. Mercury vapor was one of the chief contaminants to guard against. This was effectually kept out of the experimental tube by the two liquid air traps which connected through a stopcock. Every precaution was taken to ensure the purity of the nitrogen since the effect of impurities is uncertain.

The experimental tube was thoroughly baked out after evacuation by wrapping it with resistance wire and heating it electrically to 300°C for several hours with the pumps running. The metal box within the tube was then heated by an induction furnace until free of occluded gases, and finally the filament was glowed. Nitrogen was then introduced from the nitrogen reservoir until the desired pressure of nitrogen was obtained. A glow could then be developed by suitable adjustment of the filament current and box potential. The spectrum of the glow in the equipotential space within the box was then photographed at various potentials.

### RESULTS

Due to the fact that an arc could not be maintained in pure nitrogen below about 17 volts, this investigation was limited to the critical potential for the negative bands. A series of spectrograms was taken at an interval of a volt from 18 to 23 volts. The nitrogen pressure varied from .085 to .140 mm; it could not be kept constant because of the continual absorption in the experimental tube. The following table gives the plate current and the photographic exposure for the six spectrograms.

Voltage	Plate current	Exposure
18.0	70 m-amp.	4 hr
19.0	120	2
20.0	160	2
21.0	200	2
22.0	200	1½
23.0	200	1½

The wave-lengths of the negative bands identified are given in the following table, arranged according to groups.

Group 1	Group 2	Group 3	Group 4
5228A	4708A	4278A	3914A
5151	4651	4326	
	4599	4199	
		4167	

In each group the bands decrease in intensity from the top of the column down. The band  $\lambda 4278$  is photographically the brightest of the negative bands on our plates.

As we go to lower voltages the fainter bands of the negative group fade out, but on the 19 volt spectrogram one can easily identify 4708;

4278, 4236; and 3914, while there is a faint trace of 4599. On the 18 volt spectrogram the negative band 4278 is distinctly visible and there are traces of 4708 and 4236.

The first positive group and all the bands of the second positive group listed by Kayser in his *Handbuch der Spektroskopie* between  $\lambda 3900$  and  $4950$  have been found on these plates. Two bands of the second positive spectrum,  $4649$  and  $4200$ , overlap or at least lie so close to two of the negative bands listed above as to be indistinguishable from them on these plates. The positive band  $4649$  is not very intense, however. Both of the corresponding negative bands, namely  $4651$  and  $4199$ , give evidence of their presence by the increase in intensity of the superposed bands as we go from 18 volts to 23 volts.

The fact that nothing but the nitrogen bands appeared with sufficient intensity on these plates to be measured and identified is evidence of the purity of the nitrogen used.

#### DISCUSSION AND REMARKS

These results seem to indicate that the negative band spectrum appears as a whole at the ionization potential of nitrogen or somewhere between that and 18 volts. The fact that some of the weaker bands are not present on the spectrograms at the lower voltages seems to be due to the fact that they have become too weak to be recorded on the photographic plate or in other words that they have faded out.

Attempts to obtain a spectrogram at 17.0 or 17.5 volts in pure nitrogen were not successful because that is too near the minimum potential at which an arc can be maintained. It was found that at 0.1 and 0.2 mm the lowest voltage at which an arc could be maintained in pure nitrogen was 17.0 volts, while at 0.63 mm the lowest voltage was 16.5.

All the voltages mentioned thus far have been uncorrected voltages. The voltage correction was obtained by filling the experimental tube with mercury vapor, running ionization curves, and taking the ionization potential of mercury vapor as 10.4 volts. The ionization potential of mercury vapor according to these curves was 10.65 volts, which makes the voltage correction  $-.25$  volt.

In work of this kind the mean free path of the electrons should not be less than the distance from filament to box. According to Wahlin<sup>6</sup> the mean free path of the electrons in nitrogen is .000131 cm at a pressure of 760 mm. This is about 2.7 times the kinetic theory value. Since the pressure of the nitrogen in these experiments was about .1 mm, it follows, using Wahlin's value, that the mean free path of the electrons in our

<sup>6</sup> Wahlin, *Phys. Rev.* 23, 169 (1924).

case was about 10 mm, which was five times the distance from filament to box.

Tests were made several times to detect the presence of oscillations in the arc by the use of a peak voltmeter, but no evidence of oscillations was ever detected in this way in spite of the fact that noises could sometimes be heard in telephone receivers connected across the gap between anode and filament.

Our results are in accord with those of Duffendack and Duncan,<sup>4</sup> who found that the "negative bands appear above the ionizing potential" of nitrogen. They are also in accord with the observations of Foote, Mohler, and Meggers.<sup>3</sup> They are not in accord, however, with the results of Bloch and Bloch,<sup>1</sup> who found that the negative band 3914 appeared at 21 or 22 volts. On our plates the band 3914, though never very intense because it is in a region where the glass of the spectrograph absorbs a considerable part of the light, can still be identified at 19 volts.

In conclusion the writer wishes to acknowledge his indebtedness to Dr. C. B. Bazzoni, who suggested this investigation and under whose direction it was carried out.

RESEARCH SECTION,  
RANDAL MORGAN LABORATORY,  
UNIVERSITY OF PENNSYLVANIA.  
August 24, 1925.



## THE IONIZATION OF NITROGEN BY ELECTRON IMPACT AS INTERPRETED BY POSITIVE RAY ANALYSIS

BY T. R. HOGNESS AND E. G. LUNN

## ABSTRACT

Using an apparatus previously described in which ions formed by impact of electrons of energy  $(V_1 + V_2)$ , or by secondary processes, are pulled from the ionization chamber by the field  $V_3$  and then analyzed magnetically by Dempster's method, the relative numbers of ions of type  $N_1^+$  and  $N_2^+$  are measured for various pressures and voltages. At low pressures (less than  $10^{-5}$  mm) only  $N_2^+$  was observed; as the pressure was increased the percentage of  $N_1^+$  increased regularly and reached 60 at .006 mm. The percentage of  $N_1^+$  was markedly greater when helium at a relatively high partial pressure was present. Below 24 volts, no  $N_1^+$  ions were produced, although  $N_2^+$  ions appeared with  $(V_1 + V_2)$  greater than 17 volts. These  $N_2^+$  ions must therefore be stable toward collisions, while above 24 volts  $N_2^+$  ions are produced which may be disrupted on collision to form  $N_1^+$  ions. The critical potentials for nitrogen of 16.95 and 24.6, then, correspond to the formation of  $N_2^+$  (stable) and  $N_2^+$  (unstable).  $N_1^+$  ions are therefore produced only by dissociation of unstable  $N_2^+$  ions. The percentage of  $N_1^+$  was found to be independent of the field  $V_3$  from 2.7 to 27 volts, hence the dissociation of an unstable  $N_2^+$  ion is independent of its speed over this range.  $N_1^{++}$  ions are not produced at all below 500 volts. The  $N_2^-$  ions found by Smyth were present but too weak to be studied. A diagrammatic representation of the electrons distributed in the two types of  $N_2^+$  ion is suggested in accordance with the ideas of G. N. Lewis. Correlation with spectroscopic evidence indicates that the negative bands are emitted by the stable ions.

THE method for the positive ray analysis of the products of electron-impact ionization of gases previously described<sup>1,2</sup> in its application to hydrogen is here used to study the ionization of nitrogen.

*Apparatus and method.* Electrons from the oxide-coated platinum filament *E* (Fig. 1) are accelerated by the field  $(V_1 + V_2)$  into the ionization chamber *H*. The ions formed there by the primary process of electron impact and by secondary processes, are accelerated by the small field  $V_3$ , then by the large analyzing<sup>3</sup> field  $V_4$ . Those that pass through the slit *B* enter the analyzing magnetic field where they are bent through the arc of a circle; the ion beam is focused on to the slit *M* and the electrometer collecting plate by varying either  $V_4$  or the magnetic field.

<sup>1</sup> Hogness and Lunn, Proc. Nat. Acad. Sci. **10**, 398 (1924).

<sup>2</sup> Hogness and Lunn, Phys. Rev. **26**, 44 (1925).

<sup>3</sup> Dempster, Phys. Rev. **11**, 316 (1918).

The nitrogen was prepared by the action of bromine-water on aqueous ammonia and was purified with solid potassium hydroxide, liquid air, and phosphorus pentoxide.

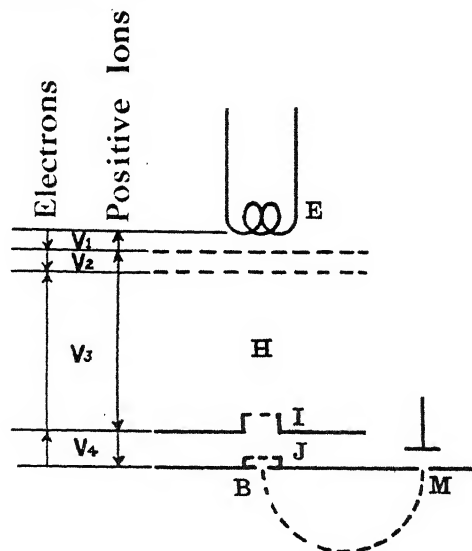


Fig. 1. Diagram showing method of analysis of ions.

*Positive ions.*  $N_2^+$  and  $N_1^+$  were the only positive ions found. It may be recalled that in the ionization of hydrogen by electron impact the

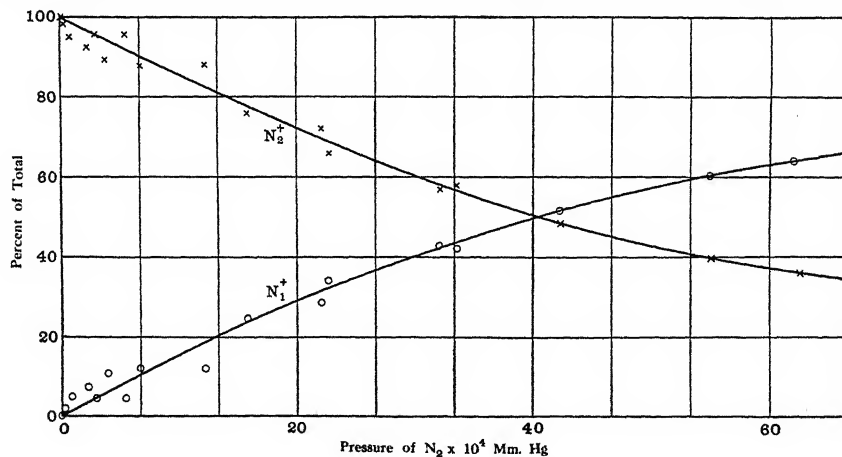


Fig. 2. Percentage of  $N_1^+$  and of  $N_2^+$  as a function of pressure.

formation of the singly-charged molecular ion is the primary process.<sup>4,5,2</sup> That, analogously, the formation of  $N_2^+$  is the primary process and that

<sup>4</sup> Dempster, Phil. Mag. 31, 438 (1916); Phys. Rev. 6, 651 (1916).

<sup>5</sup> Smyth, Phys. Rev. 25, 452 (1925), and references there cited.

$N_1^+$  is formed by collision of unstable  $N_2^+$  with gas molecules, is shown by Figs. 2 and 3. In Fig. 2 the percentage of  $N_1^+$  and  $N_2^+$  as measured by the relative peak intensities is plotted against the pressure of nitrogen. It is evident that the percentage of  $N_1^+$  extrapolates to zero at zero pressure;  $N_1^+$  can therefore be formed only by secondary collision. Confirmatory experiments failed to show any trace of  $N_1^+$  at pressures of less than  $10^{-5}$  mm, although the intensity of  $N_2^+$  was still large.

The conclusion that  $N_1^+$  is formed by collision is further confirmed by the results of a study of the relative ionic intensities in mixtures of helium and nitrogen. The intensity peaks  $N_1^+$  and  $N_2^+$  were first obtained for a low pressure (Fig. 3A); helium was then mixed with the nitrogen in the reservoir, the partial pressure of the latter being therefore the same

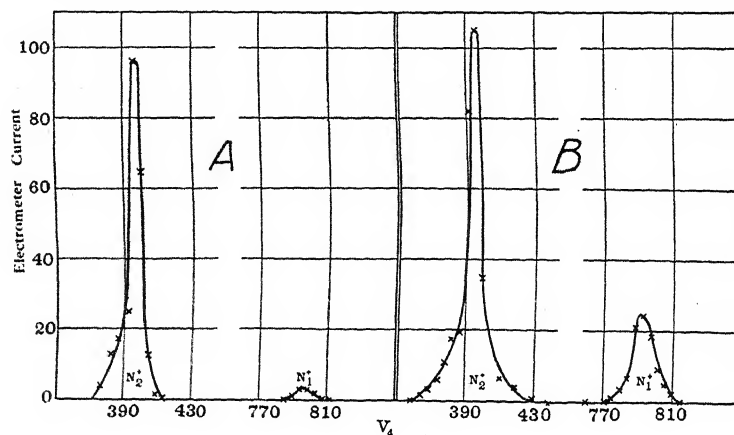


Fig. 3. Peaks obtained (A) with pure nitrogen, (B) with a mixture of nitrogen and helium.

as its previous total pressure, and the intensity peaks were again measured with other conditions the same. The percentage of  $N_1^+$  was appreciably greater (Fig. 3B). The presence of the helium increased the chance of collision of the unstable  $N_2^+$  and its consequent disruption:



The experiments of Figs. 2 and 3 were made with 84-volt electrons.

Now consider, however, the experimental results presented in Fig. 4 in which the percentage of  $N_1^+$  and  $N_2^+$  is plotted against the corrected voltage of the impact electron ( $V_1 + V_2$ ). (The smaller figure relates to another experiment extending to higher voltages.) From 17-24 volts no  $N_1^+$  ions were formed. Similarly, Fig. 5A shows the results of an intensity-peak experiment made with 23-volt electrons at a high pressure, which

normally favors the formation of  $N_1^+$ , yet no evidence thereof is shown. Fig. 5B was obtained with 84-volt electrons under the same conditions, except that the filament current was reduced to make the  $N_2^+$  intensity

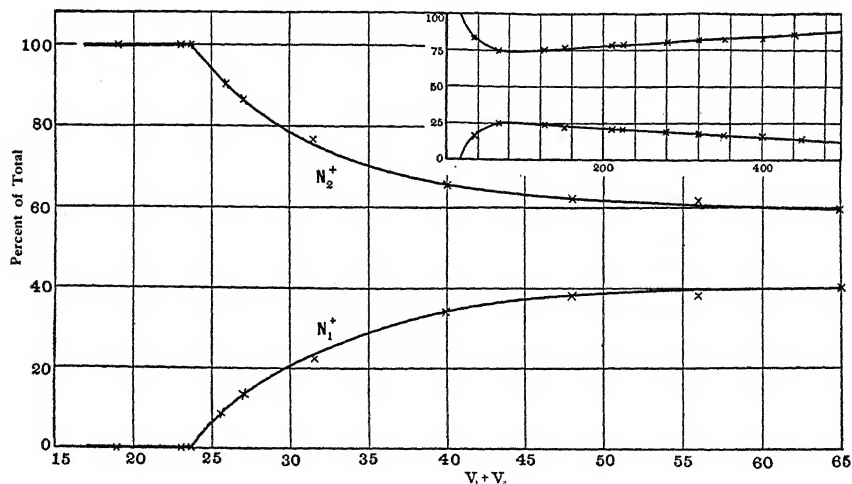


Fig. 4. Variation in the relative numbers of  $N_1^+$  and  $N_2^+$  ions with energy of impact electrons.

comparable with that in Fig. 5A. Now, Figs. 2 and 3 give evidence that  $N_1^+$  is formed only by collision of  $N_2^+$  with gas molecules; Figs. 4 and 5

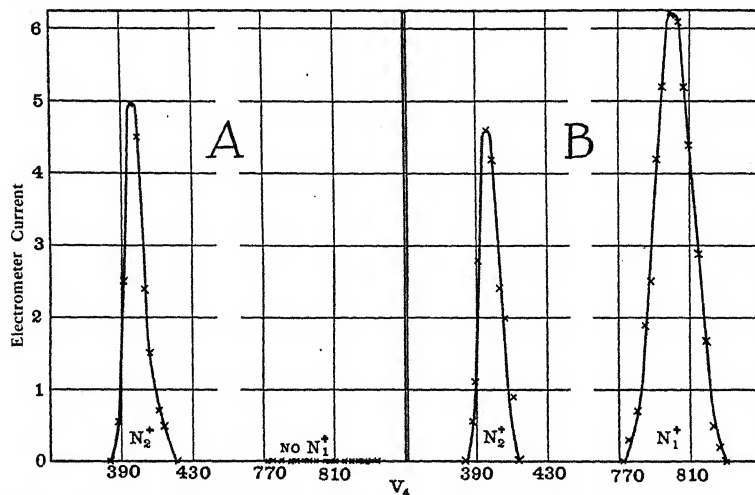


Fig. 5. Peaks obtained (A) with 23-volt and (B) with 84-volt impact electrons.

give evidence that  $N_1^+$  is not formed below 24 volts. There are, therefore, two kinds of  $N_2^+$  ions: the unstable form, which is produced by impact

electrons of energy greater than 24 volts and is disrupted on collision with gas molecules; the stable modification, which has energy equivalent to 17-volt electrons and is not disrupted by such collision. The critical potentials of 17 and 24 volts for the formation of the stable and unstable  $N_2^+$  ions respectively are the means of six determinations made in essentially the manner previously described<sup>2</sup> for hydrogen with the use of helium as the calibrating gas. The disappearing-potential curves  $N_1^+$ ,  $N_2^+$  and  $He^+$  (Fig. 6) when extended to higher voltages approach the same "saturation" intensity; this, as was previously shown, is a necessary condition for the more accurate determination of ionization potentials by this method.

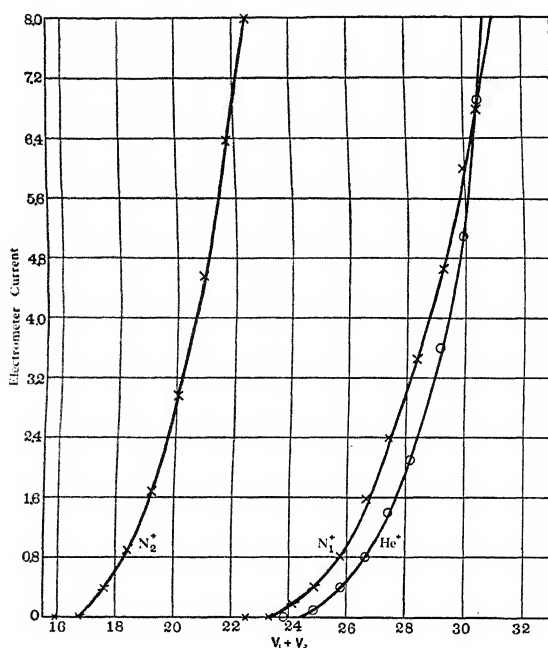


Fig. 6. Variation of intensity of peaks  $N_2^+$ ,  $N_1^+$  and  $He^+$  with energy of impact electrons.

Study of the relative intensities of  $N_1^+$  and  $N_2^+$  as a function of  $V_3$  showed that over a range of 2.7 to 27 volts the percentage of  $N_1^+$  is independent of  $V_3$ . The dissociation of the unstable  $N_2^+$  ion is therefore independent of its speed over this range.

*Negative ions.*  $N_2^-$  was the only negative ion detected. Under all conditions of pressure, filament current, etc., studied, its intensity was very small—too small to make feasible a study of its origin.

## DISCUSSION

The principal conclusions of Smyth<sup>6</sup> from his study of the ionization of nitrogen may be briefly summarized as follows: (1) The ions  $N_2^+$ ,  $N_1^+$  and  $N^{++}$  are formed as the result of primary ionization by impact electrons at ionization potentials of (16.9),  $27.7 \pm 0.8$  and  $24.1 \pm 1.0$  volts, respectively; (2) the percentage of  $N_1^+$  and  $N^{++}$  ions increases sharply at 350-400 volts; and (3) negatively charged molecular ions are formed. Smyth's conclusion that  $N_1^+$  is formed directly by electron impact is made untenable by the facts presented above. In the light of his subsequent work on hydrogen<sup>5</sup> it seems probable that the ion of apparent  $m/e=7$  which Smyth ascribed to  $N^{++}$  is one of the type  $N_{2-1}^+$ , namely, an ion  $N_2^+$  which dissociated after it had fallen through the full analyzing field  $V_4$ . This view he has since hinted at.<sup>7</sup> The ionization potentials attributed by him to the formation of  $N_1^+$  and  $N^{++}$  should have been the same according to this view. Smyth's value of  $27.7 \pm 0.8$  volts should then be considered as spurious, while the 24.1 value agrees with that found by us, within experimental error. Traces of an ion having an apparent  $m/e=7$  were found also in the present work, but only at the highest pressures employed. They could be formed by disruption of  $N_2^+$  ions in the region between the gauge  $J$  and the slit  $B$  (Fig. 1). The insert of Fig. 4 shows no evidence of the abrupt increase in the percentage of  $N_1^+$  at 350-400 volts found by Smyth.

The several determinations of the critical potentials of nitrogen<sup>8</sup> all show a critical point near 17 volts. The accurate measurements of Brandt<sup>9</sup> gave 16.95 volts as its value, and in addition show two higher potentials of 24.6 and 29.9 volts. In the light of the present work the 16.95 and 24.6 volt potentials are those for the formation of the  $N_2^+$  (stable) and  $N_2^+$  (unstable) respectively.

In studying the synthesis of ammonia from nitrogen and hydrogen in the low-voltage arc, Storch and Olson<sup>10</sup> found an abrupt increase in the amount of ammonia with 23-volt impact electrons. The approximate coincidence of this critical potential with that found above suggests that the sharp increase is due to the formation and disruption of the unstable  $N_2^+$  ion.

<sup>6</sup> Smyth, Proc. Roy. Soc. 104 A, 121 (1923).

<sup>7</sup> Smyth, J. Franklin Inst. 198, 795 (1924).

<sup>8</sup> For a summary of these see Compton and Mohler, Bull. Nat. Res. Council, vol. 9, part 1, Critical Potentials.

<sup>9</sup> Brandt, Zeits. f. Physik 8, 32 (1921). See also Franck, *ibid.* 11, 155 (1922).

<sup>10</sup> Storch and Olson, J. Am. Chem. Soc. 45, 1605 (1923).

Studies of the excitation of the spectra of nitrogen by impact electrons have shown that the negative bands appear at about 20 volts,<sup>11</sup> and that the line spectrum does not appear much below 30 volts.<sup>12</sup> Presumably, then, these negative bands are due to the stable configuration of the  $N_2^+$  ion. The critical voltage of 30 for the appearance of the line-spectrum is in reasonable agreement with the ionization potential for the formation of the unstable  $N_2^+$  ion when the question of spectroscopic intensity is considered.

The effect of helium in increasing the percentage of  $N_1^+$  as noted above is in agreement with the observations of Merton and Pilley<sup>13</sup> on the effect of helium on the spectrum of nitrogen. The difference between the effects of argon and helium in exciting the line spectrum may be ascribed to the

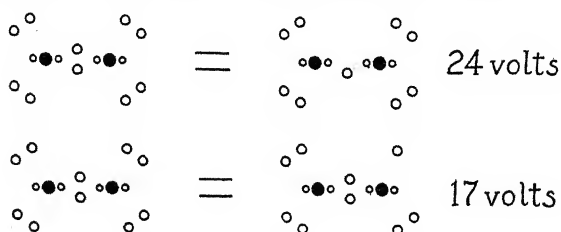
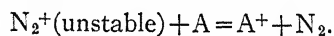


Fig. 7. Diagrammatic representation of the ionization of the two types of  $N_2^+$  ions, in accordance with the ideas of G. N. Lewis.

relatively lower ionization potential of argon and to collisions of the second kind<sup>14</sup> in which argon is ionized by the  $N_2^+$  (unstable) ion



A probable explanation of the two kinds of  $N_2^+$  ions is that two types of electrons are concerned in the ionization processes here studied. The electron removed at 17 volts is a non-bonding electron, and the  $N_2^+$  ion formed by its removal is stable; the electron removed by impact electrons of greater than 24 volts is, by analogy with the  $H_2^+$  ion, a bonding one, the removal of which forms the unstable  $N_2^+$  ion. Adopting the general scheme of the two-electron bond and the pairing of electrons proposed by G. N. Lewis,<sup>15</sup> the formation of the two types of  $N_2^+$  ions may be represented by the diagrammatic equations given in Fig. 7 where there are

<sup>11</sup> L. Bloch and F. Bloch, *Compt. Rend.* **170**, 1380 (1920); **173**, 225 (1921); Duffendack, *Astro. J.* **61**, 209 (1925).

<sup>12</sup> Duffendack, *Phys. Rev.* **20**, 665 (1922).

Duffendack and Duncan, *ibid.* **23**, 295 (1924).

<sup>13</sup> Merton and Pilley, *Proc. Roy. Soc.* **107A**, 411 (1925).

<sup>14</sup> Klein and Rosseland, *Zeits. f. Physik* **4**, 46 (1921);

Franck, *ibid.* **9**, 259 (1922).

<sup>15</sup> G. N. Lewis, "Valence and the Structure of Atoms and Molecules," Chemical Catalog Co., New York, 1923.



four non-bonding electrons for each atom in the molecule, all of which are at the same energy level. Any difference of energy in the two pairs in each atom as proposed by Stoner<sup>16</sup> would be too slight to be detected by the present method.

Studies of the dissociation of nitrogen<sup>17,18</sup> confirm the chemical evidence as to its stability. Langmuir's experiments on the dissociation of nitrogen by incandescent tungsten led him to estimate the heat of dissociation as greater than 10 volts. This fact, together with the great chemical stability, precludes the possibility of the  $N_2^+$  ion formed at 17 volts dissociating unless the ionization potential of the nitrogen atom is very low. Eucken<sup>19</sup> has recently calculated the heat of dissociation of nitrogen to be 19.1 volts, a value higher than that indicated by the present experiments.

The similarity in the ionization of nitrogen and oxygen found by Smyth<sup>20</sup> naturally suggests that the processes of ionization are similar. Experiments to investigate this are in progress.

DEPARTMENT OF CHEMISTRY,  
UNIVERSITY OF CALIFORNIA.  
September 5, 1925.

<sup>16</sup> Stoner, *Phil. Mag.* **48**, 719 (1924); also Smith, *Chem. and Ind.* **43**, 323 (1924).

<sup>17</sup> Langmuir, *J. Am. Chem. Soc.* **34**, 860 (1912); Langmuir and Mackay, *ibid.* **36**, 1708 (1914); Langmuir, *ibid.* **37**, 417 (1915).

<sup>18</sup> Duffendack and Compton, *Phys. Rev.* **23**, 583 (1924).

<sup>19</sup> Eucken, *Ann. der Chem.* **440**, 111 (1924).

<sup>20</sup> Smyth, *Proc. Roy. Soc.* **105A**, 116 (1924).

## STRIATED DISCHARGE IN HYDROGEN

BY ARTHUR BRAMLEY

## ABSTRACT

*Potential distribution, electron concentration and mean electron energy at eleven points were determined for a discharge through a tube 15 cm long at pressures of .625, .20, .09 and .02 mm, using Langmuir's probe method. The total potential difference was 270-300 volts. The potential dropped to a minimum within 2 mm of the cathode, of 125, 60 and 20 volts for pressures .20, .09 and .02 respectively, giving a reverse gradient in a region 1 to 2 cm long through which the current must have been carried by diffusion of positive ions and electrons. The gradient was also reversed at the anode edge of a striation for pressures of .20 and .09 mm—the lower pressure .02 mm gave a uniform positive column. The electron concentration reached a maximum 1 to 2 cm in front of the cathode; the values, in general, are lower the higher the pressure. The mean electron energy decreases sharply at the cathode to a minimum of 1 to 2 volts, then rises gradually to about 10 volts at the beginning of the positive column; it also reaches 10 volts at a striation. Such electrons have sufficient energy to cause the ionization which is associated with the luminosity in the positive column. The anode drop within 2 mm was only 5 to 15 volts, the potential distribution depending on the position of the nearest striation.*

ALTHOUGH a large amount of work has been done on the striated discharge in monatomic gases, very little has been done recently on the discharge in diatomic gases at low pressures, where the presence of various kinds of ions renders the interpretation of the results obtained more difficult.

The method employed in this investigation is the one suggested by Langmuir. If a wire is introduced into the discharge and maintained at a negative potential with regard to the surrounding space, a positive space charge arises which limits the positive ion current reaching the wire. As the potential of the wire is raised, electrons reach the wire against the potential of the field until the resultant current becomes zero. Finally, when the wire exceeds the potential of the space, positive ions are prevented from reaching the wire, so that it becomes surrounded with a negative space charge. Therefore when the potential of the wire becomes equal to that of the space surrounding it, a change in the law governing the current to the wire must take place.

If there is a Maxwellian distribution of velocity the current reaching the wire can be expressed in the following form

$$I = N_0 e \sqrt{(e\bar{v}/3\pi m)} e^{-3(v_0 - v)/2\bar{v}} \quad (1)$$

where  $I$  is the current to the exploring electrode,  $N_0$  the concentration of the electrons,  $m$  and  $e$  the mass and charge of an electron,  $\bar{v}$  the average velocity of the electron, expressed in equivalent volts,  $v$  the potential of the wire and  $v_0$  the potential of the space. From this equation it follows that

$$\log I = -(3/2) (v_0 - v)/\bar{v} + \text{const.}$$

so that if  $\log I$  is plotted against  $v$  a straight line ought to be obtained, whenever there is a Maxwellian distribution of velocities. The slope of this curve ( $\tan \theta$ ) enables us to find the average velocity of the electrons at once, for  $\tan \theta = 3/2\bar{v}$ . The potential of the space will be the potential at which the graph of  $\log I$  plotted against  $v$  begins to deviate from a straight line.

When  $v_0 - v = 0$  the equation simplifies to the form

$$I = N_0 e \sqrt{(e\bar{v}/2\pi m)}$$

so that, knowing  $\bar{v}$  from the slope of the curve, we can compute the concentration of the electrons.

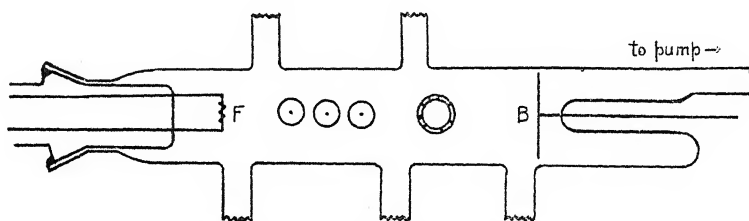


Fig. 1. Discharge tube with exploring electrodes inserted through side tubes.

A diagram of the apparatus used in this experiment is given in Fig. 1. The filament  $F$ , which serves as a hot cathode to maintain the discharge at low voltages, and the anode  $B$  were fixed with respect to the main tube of 3.8 cm diameter. The exploring electrodes, of which there were eleven placed at different positions in the path of the discharge, were each of 4 mil (.1 mm) tungsten wire covered with glass to within a few millimeters of the end which was placed as near the axis of the discharge as possible. The object of using the eleven fixed electrodes in preference to a moving cathode-anode system and a single electrode was to enable a series of readings of the current to be taken without altering conditions in the discharge.

Fig. 2 gives a few typical  $\log I$  vs potential curves for different conditions in the tube. Curves 1 and 2 represent the type obtained near the cathode where we have relatively high speed electrons together with slow ones. In this type of curve, we find first a linear part with small

slope which represents large energy since the energy varies inversely as the slope, curving upwards as the slow speed electrons reach the electrode against the space charge sheath; this second part which becomes also a straight line with much greater slope than the first changes into a parabolic curve when the potential of the space is reached. Curve 3 gives the form of curve obtained in the positive column; the breaks in this curve at 12 volts apart which are found above the potential of the field have received as yet no adequate explanation. The breaks in the

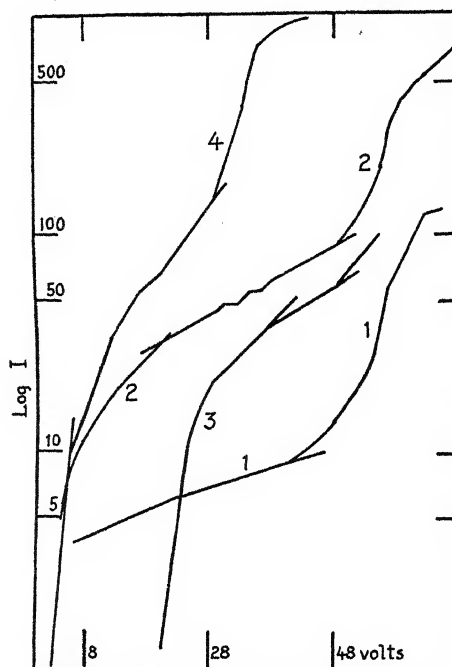


Fig. 2. Typical  $\log I$  vs potential curves for exploring electrodes.

curves fall about 16 and 12 volts apart on the average and may represent the ionization of the hydrogen molecule and atom respectively. Curve 4 is typical of the curves obtained at high pressure ( $p = .625$  mm) where the mean free path is so small that different conditions from those obtained at the other pressures seem to be present.

In Fig. 3 the distribution of potential, the log of the concentration of the electrons and the mean energy of the electrons for the different points in the discharge from cathode to anode where the exploring electrodes are situated are given for pressures of .625, .20, .09 and .02 mm. Below .015 mm no discharge would pass through the gas although the potential across the tube was increased from 270 to 750 volts. At .02 mm it was

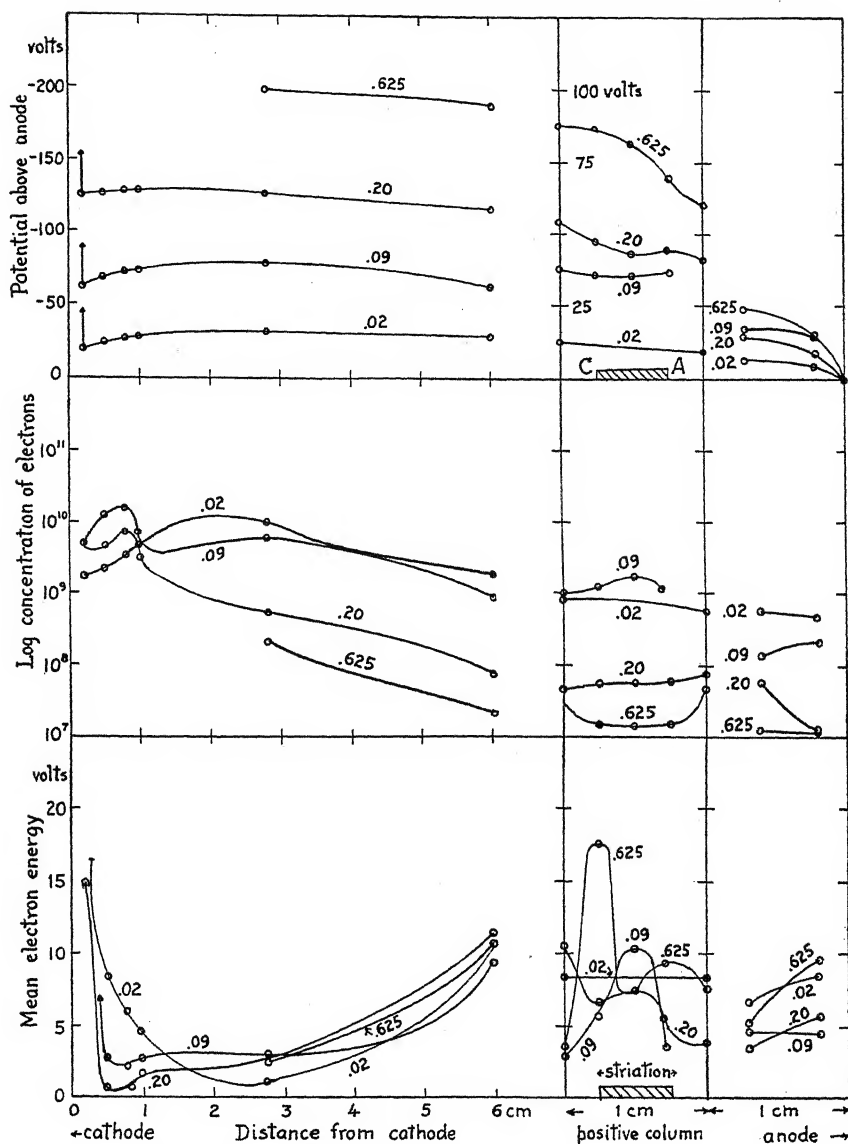


Fig. 3. Potential, logarithm of concentration of electrons, and mean electron energy at different parts of the discharge within 6 cm of the cathode (left), in a striation (middle) and within 1 cm of the anode (right) where the eleven fixed exploring electrodes were situated, for pressures of .02, .09, .20 and .625 mm. For the lowest pressure there were no striations, merely a uniform positive column. In the positive column the indicated position of the striation is only approximate; the maximum mean electron energy occurs near the cathode edge in each case.

found impossible to maintain a striated discharge in the gas through the same potential range. The explanation of this is probably connected, as we shall see, with the condition of the discharge in the neighborhood of the cathode.

We shall first consider the conditions near the cathode and in the region of the Faraday dark space. As the pressure of the gas in the tube is diminished the cathode fall becomes a greater fraction of the total potential applied to the tube until a pressure is finally reached such that the electric intensity is reversed in the Faraday dark space. In this case there is a group of higher speed electrons proceeding from the cathode together with the group of slow electrons which have a large concentration in this region. The higher speed electrons evidently cause continual ionization which results in the large concentration of low speed electrons, the current in the tube being carried by diffusion of positive ions toward the cathode. At high pressures the concentration of electrons is much smaller and the current is due to the electric field; in this case the first term of the equation

$$F = N_0 e E - kT \frac{dN_0}{dx}$$

predominates while at low pressures (since both  $N$  and  $E$  are very small as compared with  $dN/dx$  and  $kT$ —see Fig. 3), the last term (which is due to diffusion) governs the conditions in the discharge. In this equation  $F$  is the force on the ions,  $E$  the electric field and  $kT$  is two-thirds the kinetic energy of the ions.<sup>1</sup> If the pressure is lowered still further, the intensity of ionization must become smaller until a point is reached where the concentration of positive ions is not sufficient to maintain the discharge.

From the concentration and average velocity of high speed electrons for the pressure of .02 mm, a calculation of the total emission from the filament (using Eq. 1) gave results in approximate agreement with the total current in the tube. The total emission calculated was 50 milli-amp. while the total current in the tube as calculated from the measured concentrations was 35 milli-amp. In the calculation the higher speed electrons were assumed to move radially from the cathode without taking into account (1) the possibility of collisions before reaching the electrode, (2) ionization in the region of the space charge sheath surrounding the electrode, and (3) loss due to collisions with the walls of the tube, since the mean free path was nearly four times the radius of the tube.

<sup>1</sup> A thorough discussion of the effects of the electric field intensity and diffusion on the type of discharge has been given by K. T. Compton, Louis A. Turner and W. H. McCurdy, *Phys. Rev.* **24**, pp. 597-615 (Dec. 1924).

As we move down the tube, the average energy of the electron increases until, as we approach the head of the positive column, the energy becomes nearly equal the ionization potential of hydrogen. In the positive column, the fall in potential over a striation decreased from 30 volts to about 11 volts as the pressure decreased from .625 mm to .09 mm; at the same time, however, the average velocity of the electrons within the striation did not decrease appreciably. Throughout this range of pressure a group of electrons, with average velocity over 10 equivalent volts, was found in the striation toward the cathode side. These electrons must cause the ionization which results in the luminous striated discharge since accumulative ionization has not been found in hydrogen. When the pressure was still further lowered to .02 mm the positive column was uniform and the average energy of the electrons was constant at about 8.4 volts throughout this region.

At the anode the fall of potential within 2 mm never exceeded 15 volts and seemed to be determined by the position of the last striation relative to the anode. In the case of the uniform column (.02 mm) the fall of potential was only about 5 volts.

In the positive column, the character of the discharge at high pressures is determined by the conductivity due to the large electric gradient while at low pressures since the electric field is very small and even negative in some places, the diffusion of the electrons and ions plays a more fundamental rôle than the electric field.

In conclusion, I wish to express my gratitude to Professor K. T. Compton for suggesting the problem and for his helpful suggestions during the course of the investigation.

PALMER PHYSICAL LABORATORY,  
PRINCETON, NEW JERSEY,  
June 22, 1925.



THE SECONDARY EMISSION FROM A NICKEL SURFACE  
DUE TO SLOW POSITIVE ION BOMBARDMENT

BY A. L. KLEIN

## ABSTRACT

The apparatus was arranged so that positive ions from a heated Mo strip coated with aluminum phosphate, were accelerated radially through slots in shields *A* and *B*, and a wider slot in an electrode *C* to the target *T*, from which the secondary emission to the electrode *C* was measured. The parts *A*, *B*, *C* and *T* were all concentric nickel cylinders, symmetrically placed about the emitter. If the potential of the emitter is made zero and the accelerating potential  $V_1$ , when the collector is at zero potential only reflected positives are collected. As the potential is increased, secondaries also reach it, the net negative charge increasing until a saturating potential  $2V_1$  is reached, when all negatives and no positives are collected. The percentage saturated *secondary electron emission* was found to increase approximately as the square of the primary ion energy, reaching 22 percent of the primary ion current, for primary ions of energies corresponding to 380 volts. The curves show that large numbers of *reflected positive ions* have energies between zero and two volts, and there is also a group of reflected positive ions with energies approximately 0.9 of the primary energy.

THE problem of the secondary emission from metallic surfaces due to positive ion bombardment has been attacked by several workers. Among others Fuchtbauer,<sup>1</sup> Cheney,<sup>2</sup> Baerwald,<sup>3</sup> Hahn,<sup>4</sup> and Baderau<sup>5</sup> have made important contributions.

The apparatus used in this work consisted of a number of coaxial nickel cylinders arranged symmetrically around a central molybdenum positive ion emitter. The emitter consisted of a strip of molybdenum 0.13 mm thick, 2.5 mm wide, and 12 mm long; this strip was bent into an open circular band, and heated by passing an electric current through it. The emitter was activated by covering it with a thick layer of  $\text{AlPO}_4$ . The innermost cylinder designated in Fig. 1 as *A*, was 10 cm long and 3 cm in diameter, and has a slot 1.5 mm wide cut around its center, except in three places where legs were left to hold the two parts of the cylinder together. The ends of the tube were closed by means of nickel caps. The next cylinder *B* is 5 cm long and 3.5 cm in diameter. It has a slot around its center aligned with the one in *A*, but three mm wide. The two collect-

<sup>1</sup> Fuchtbauer, Phys. Zeits. 7, 153 and 748 (1906); Ann. der Phys. 23, 308 (1907).

<sup>2</sup> Cheney, Phys. Rev. 10, 335 (1917).

<sup>3</sup> Baerwald, Ann. der Phys. 41, 643 (1913); 60, 1 (1919); 65, 167 (1921).

<sup>4</sup> Hahn, Zeits. f. Phys. 14, 335 (1923).

<sup>5</sup> Baderau, Phys. Zeits. 25, 137 (1924).

ing cylinders  $C'$  and  $C''$  are each 4 cm in diameter and 2.5 cm long. The distance between them is 13 mm. The fourth cylinder  $T$  is the target and is 5 cm in diameter and 5 cm long. This cylinder is pierced with an observation hole approximately 8 mm in diameter. This cylinder has attached to it a constantan-tungsten thermocouple.

The apparatus was inclosed in a Pyrex glass bulb and evacuated by means of a two stage mercury diffusion pump backed by a Cenco Hyvac pump. Liquid air was kept on the apparatus during observations and the pressure was measured by means of a McLeod gauge. Before taking any observations the target was always glowed out at  $1000^{\circ}\text{C}$  for three or four minutes by means of induced currents.

The electrical connections are shown in Fig. 2. The emitter  $E$  was heated by means of a large six volt storage battery. The cylinder  $B$  is grounded and the emitter is made positive; the cylinder  $A$  is made less positive than  $E$  so that part of the potential drop occurs between  $E$  and  $A$  and the remainder between  $A$  and  $B$ . The target  $T$  is connected to the cylinder  $B$  through the galvanometer  $G_1$ . The two collecting cylinders  $C'$  and  $C''$  are connected together and then through the galvanometer  $G_2$  and the variable potential  $V_3$  to the target  $T$ . Thus a positive ion on evaporating from  $E$  is accelerated through the slots in  $A$  and  $B$  and then impacts against  $T$ ; then by means of the variable potential  $V_3$  a saturation curve of the emission from  $T$  due to the impact of the positive ions upon it can be obtained.

The galvanometer  $G_1$  (Leeds and Northrup type R) has a sensitivity of the order of 1800 megohms; galvanometer  $G_2$  (Leeds and Northrup

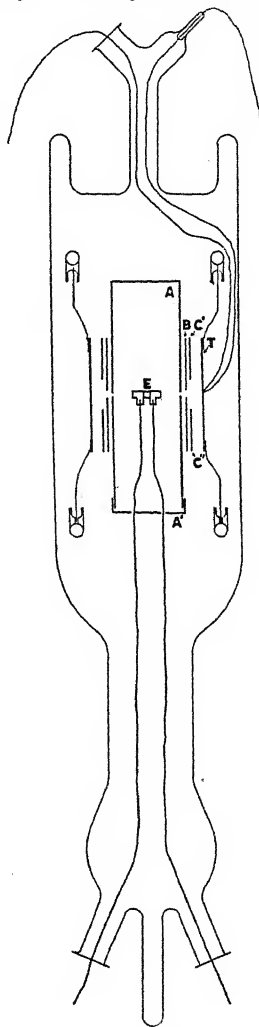


Fig. 1. Diagram of the apparatus. .

type HS) has a sensitivity of the order of 16,000 megohms. It will be noticed that  $G_1$  reads all of the positive ion current that arrives at the target or collectors, while  $G_2$  reads only the current between the collectors and the target. Consequently the reading of  $G_2$  gives for any particular voltage  $V_3$  the sum of the secondary electron emission and the secondary or reflected positive ion emission. By dividing the reading of  $G_2$  by the reading of  $G_1$  the ratio of the secondary current to the primary current is obtained.

*Method of procedure.* In taking a series of observations the target is first glowed out at  $1000^\circ\text{C}$  for a few minutes and the emitter heating current is turned on. The apparatus is then left for about 15 minutes

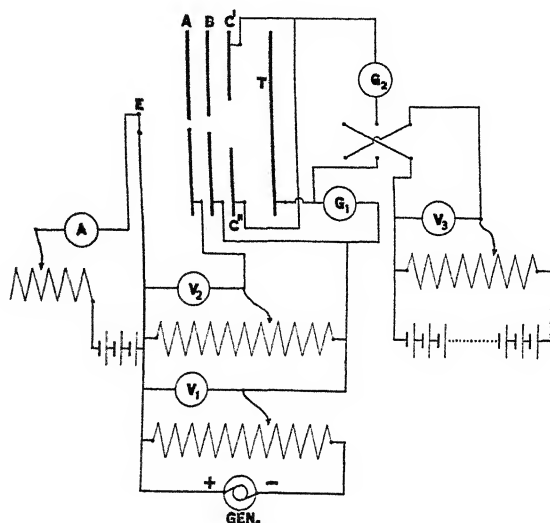


Fig. 2. Diagram of electrical connections.

until the temperature conditions become stable as shown by the thermojunction. Then the fields are applied so that the positive ions are accelerated from the emitter through the slots in  $A$  and  $B$  against the target  $T$ . Observations are started by making the collectors  $C'$  and  $C''$  negative with a potential equal to that of the positive ions incident on the target. A reading of  $G_1$  and  $G_2$  is then taken, after which the potential of the collectors is decreased somewhat towards zero, and another reading is taken. This is repeated until the potential reaches zero, and then the potential is increased in the positive direction by small increments until it reaches a positive voltage equal to twice the voltage of the incident positive ions. If the ratio of the readings of  $G_2$  to  $G_1$  is plotted against the potential of the collectors, a saturation curve is

obtained for the current between the collectors and the target. The curves obtained in this way for various voltages of positive ions are shown in Figs. 3, 4, and 5. During observations the vacuum was always

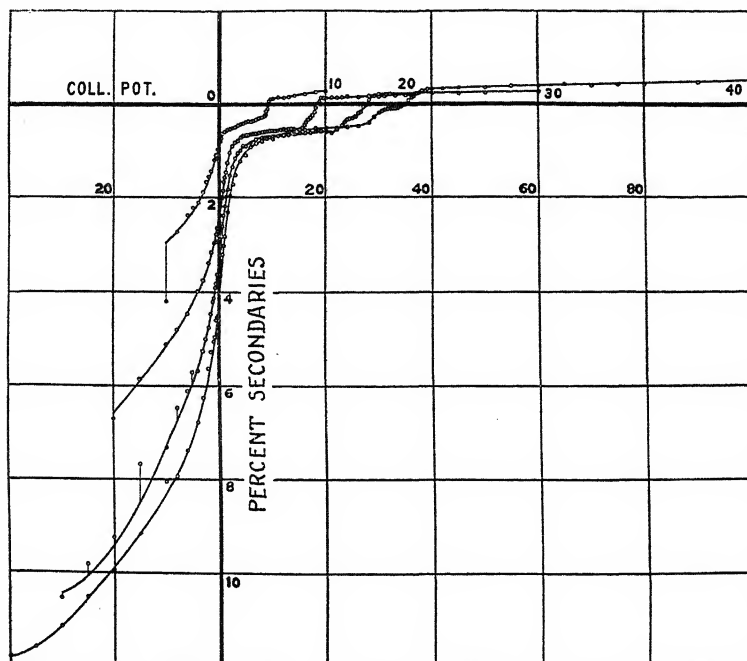


Fig. 3. Curves for accelerating potentials of 10, 20, 30 and 40 volts.

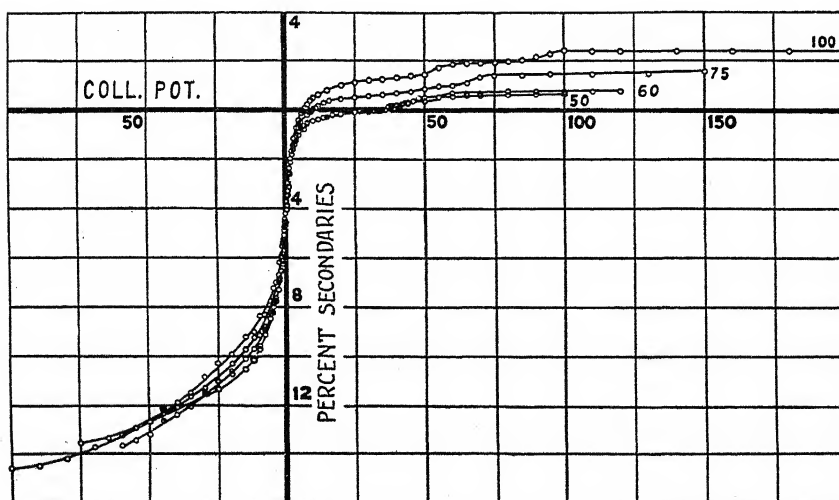


Fig. 4. Curves for accelerating potentials of 50, 60, 75 and 100 volts.

less than  $10^{-5}$  mm of Hg. The temperature of the target was always between  $160^{\circ}\text{C}$  and  $180^{\circ}\text{C}$ .

The positive ions used were obtained from hot  $\text{AlPO}_4$ , and, according to Dempster,<sup>6</sup> are ions of sodium and potassium. The writer has had no opportunity to determine the constitution of the ions used, but he hopes to do so in the immediate future.

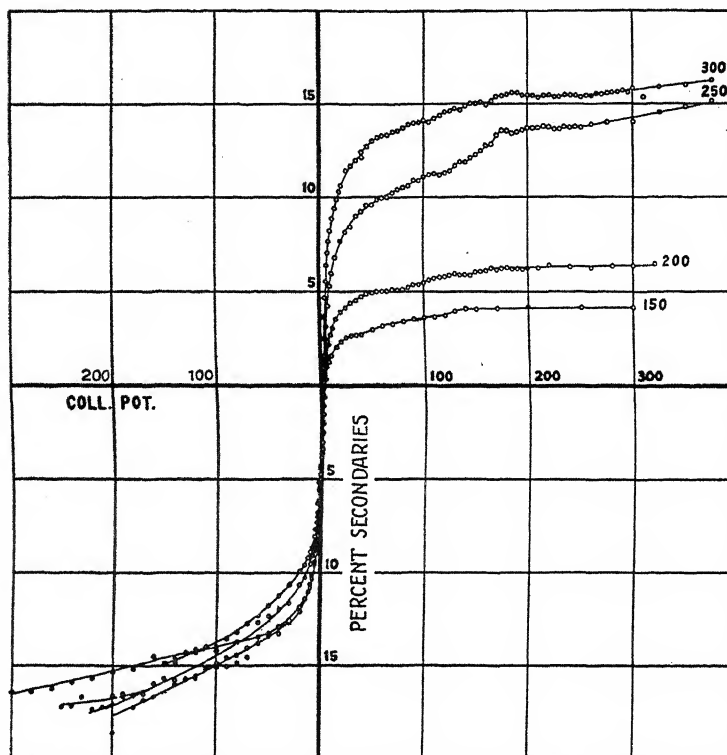


Fig. 5. Curves for accelerating potentials of 150, 200, 250 and 300 volts.

*Discussion of curves.* The saturation curves shown in Figs. 3, 4, and 5 are all plotted with the ordinates representing the percentage ratio of the secondary to the primary current. The abscissas represent the collecting potential, and the numbers at the end of the curves show the value of the primary ion energy for that particular curve. In the plots the ordinates above the axis represent secondary electron emission, those below represent reflected or secondary positive ions; the abscissas to the right represent positive collecting potentials, those to the left negative. It will be noticed that the points to the left of the y-axis are rather

<sup>6</sup> Dempster, Phys. Rev. 11, 320 (1922).

scattered and do not lie on a smooth curve as do the points to the right of the  $y$ -axis. This condition is due to the pulling of the ions out of the primary beam by the potential of the collector. As the negative collecting potential comes nearer to that of the primary beam the points scatter more and more. It is evident that curves to the left of the axis are practically identical for all of the different voltages, being simply traced further and further to the left as the voltage of the primary ions increases. There could be no object in increasing the negative potential on the collector to more than the accelerating potential, as then the collector would simply gather in the ions from the primary beam. Also it will be seen that all of the curves have strong points of inflection in the vicinity of zero volts. This large change in the value of the ordinate must mean that there are large quantities of reflected positive ions with energies in the neighborhood of zero volts, as the change is far greater than the total electron saturation current could possibly cause. After this the curves flatten out, pass through one or more new breaks, and finally reach a satisfactory saturation value when the collecting potential has the correct value. The fact that for low accelerating voltages (Fig. 3) the curves do not cross the axis until they are practically at the saturation voltage means that there are large numbers of positive ions reflected with high velocities. There seems to be one group of these reflected positive ions whose energy is about 0.9 that of the incident beam. Other groups of ions are reflected with different energies. This phenomenon serves to mask the emission of the secondary electrons so that only the curves where the energy of the incident beam is high becomes negative when the collecting potential is small.

After it was discovered that the curves all reached a saturation value when the collecting potential was higher than the primary ion potential, a curve was taken by varying the accelerating potential and maintaining the collecting potential always twenty-five percent greater. This curve (Fig. 6) shows the variation of the total secondary current with the positive ion voltage. It will be noticed that the secondary electron current is less than one percent for values below 50 volts. It increases rapidly with the primary voltage reaching a value of 22 percent at 380 volts.

There are a great many other things to be done in the future on this problem. It is proposed to study other target surfaces, to use other kinds of positive ions, and also higher voltages. For the different kinds of positive ions, hydrogen together with the series of alkali metals would be most satisfactory. Ionized hydrogen would give as a bombarding particle a proton which is the smallest known particle. The series of the

alkali metals would give as ions a series with complete K, L, M, N, and O shells. This will be very desirable, as with them the second ionizing potential will be very high, and consequently the probability that an ion will be doubly ionized is very remote. In order to determine the kind of ions that are given off by the emitter it will be necessary to use a mass spectrograph.

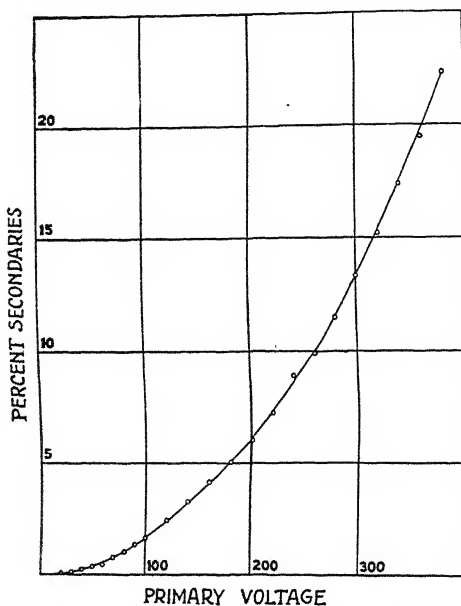


Fig. 6. Dependence of total secondary current on primary voltage.

The writer wishes to express his great indebtedness to Dr. Millikan for his help during the progress of this research. Also he wishes to thank Mr. G. A. Alles and Mr. A. L. Raymond for their help in preparing the aluminum phosphate used, and to express his deepest appreciation to Mr. W. Clancy and Mr. J. Pearson for their assistance in the design and construction of the apparatus used.

NORMAN BRIDGE LABORATORY OF PHYSICS,  
PASADENA, CALIFORNIA.

June 24, 1925.



## THE MOBILITY OF NEGATIVE IONS IN GASOLINE, HYDROGEN, AND HYDROGEN-CHLORINE FLAMES

BY PAUL E. BOUCHER

## ABSTRACT

The Hall effect method of measuring the mobility of the negative ions was used, the horizontal or vertical flame being placed in a field of 4000 to 5000 gauss. The Pt cathode was coated with sealing wax. The temperature was varied by control of the air or oxygen intake and was measured, relatively, by a Pt-PtRh couple. In a hydrogen flame the mobility increases with temperature somewhat for potential gradients over 25 volts/cm, but in a gasoline vapor flame the mobility decreases markedly. The addition of Cl, Br,  $\text{CHCl}_3$ ,  $\text{CCl}_4$ ,  $\text{NH}_4\text{Cl}$  or I (in alcohol) to the hydrogen and gasoline flame decreases the mobility, the effect being greatest for Cl and being progressively less for the other substances in the order given. In the hydrogen-chlorine flame values as low as 52 cm/sec. per volt/cm were obtained. Addition of  $\text{NaCl}$ ,  $\text{Na}_2\text{CO}_3$  or  $\text{KCl}$  increases the mobility somewhat. The highest value obtained is 5600 for hydrogen flame with  $\text{NaCl}$  sprayed in, about 30 percent higher than for a similarly sprayed gasoline flame. In explanation of these variations it is suggested that when certain substances, particularly the halogens, are added to the flame, the negative ion which is normally a free electron for the greater part of its life, tends to be attached to form a cluster so that the average period during which it is a free electron is decreased and hence the mobility also. Temperature changes and potential changes probably affect the mobility by influencing the formation of these clusters.

## INTRODUCTION

ALL measurements made on the ordinary bunsen flame agree in that the mobility of the negative ion is a thousand or more times greater than that of the positive ion. Some of the early measurements for the negative ion gave a mobility of 1000 cm per sec. per volt per cm. E. Gold<sup>1</sup> obtained two values of 8000 and 12900. H. A. Wilson<sup>2</sup> found an average value of 2450 using the Hall effect method. J. S. Watt,<sup>3</sup> using the Hall effect method, found the mobility to vary from 2700 to 1600 for potential gradients of 1 to 32 volts per cm. His results also indicate that the mobility is slightly less for salted flames than for free flames. H. A. Wilson and A. B. Bryan,<sup>4</sup> using an alternating current method of measurement at a constant frequency, found mobilities ranging from 6000 to 19300 for potential gradients from 64 to 9.4 volts per cm. By varying the frequency

<sup>1</sup> E. Gold, *Proc. Roy. Soc. A*, **79**, 43 (1906).

<sup>2</sup> H. A. Wilson, *Phys. Rev.* **3**, 375 (1914).

<sup>3</sup> J. S. Watt, *Phys. Rev.* **25**, 69 (1925).

<sup>4</sup> H. A. Wilson and A. B. Bryan, *Phys. Rev.* **23**, 195 (1924).

from  $10 \times 10^5$  to  $4 \times 10^5$ , keeping the gradient and concentration approximately constant, they were able to vary the mobility from 24000 to 8800. They found by varying any one of three factors, potential gradient, frequency of applied potential, or concentration, that the mobility of the negative ions could be made to vary through a wide range.

The character of a flame has been found by others to be profoundly influenced by the addition of chlorine or some of its compounds. Tufts<sup>5</sup> found that the introduction of chloroform into a salted flame decreased the conductivity, and also the intensity of the light emitted. Wilson<sup>6</sup> has suggested that when HCl is fed into a flame it may possibly condense on negative ions and diminish their velocity. J. Franck and P. Pringsheim<sup>7</sup> found in the hydrogen-chlorine flame that the anode fall of potential was greater than the cathode fall of potential, and from a comparison of the conductivities of the salted flame and the hydrogen-chlorine flame, concluded that free electrons could not exist in the latter flame and therefore that the negative carrier consists of an atom or a cluster of atoms. Their results seemed to indicate that the mobility of the positive ion was greater than that of the negative ion in the hydrogen-chlorine flame. S. Kalandyk<sup>8</sup> concludes from measurements of the conductivity of flames, that the mobility of the negative ion is greater in the oxy-salted flames and the mobility of the positive ion is greater in the hydrogen-chlorine flame.

The successful development of methods by which very steady hydrogen and gasoline vapor flames can be maintained made it seem desirable to investigate the various factors which appear to influence the mobility of the negative ion. In particular, the effect of temperature and the chemical nature of the flame has been studied. The following types of flame were used in this investigation: air-hydrogen, oxygen-hydrogen air-gasoline vapor, oxygen-gasoline vapor, hydrogen-chlorine. These flames were modified by varying the proportions of the constituent gases and by the introduction of the following chemicals:  $\text{CCl}_4$ ,  $\text{CHCl}_3$ , I, Br, Cl, NaCl,  $\text{Na}_2\text{CO}_3$ ,  $\text{NH}_4\text{Cl}$ , and KCl.

#### EXPERIMENTAL PROCEDURE

The Hall effect method as described in detail by Wilson<sup>2</sup> was used. The burner was placed between the pole-pieces of a Weiss electromagnet. The pole-pieces were 10 cm in diameter and 5 cm apart. Magnetic fields

<sup>5</sup> F. Tufts, *Phys. Zeits.* **5**, 76 (1904).

<sup>6</sup> H. A. Wilson, *Phil. Trans.* **A216**, 63 (1916).

<sup>7</sup> J. Franck and P. Pringsheim, *Deutsch. Phys. Gesell. Verh.* **13**, 328 (1911).

<sup>8</sup> S. Kalandyk, *Journ. de Phys.* **5**, 345 (1924).

of 4000 to 5000 gauss were used. A very steady gasoline or hydrogen flame was obtained by passing the gas into a gasometer then through an oxy-acetylene blow-pipe to the burner. The needle valves of the blow-pipe gave a very fine adjustment of both gas and air or chlorine.

Experiments were carried out on both vertical and horizontal flames. In the former the electrodes are placed one above the other; in the latter, which is a broad flat flame, the electrodes are arranged to conduct the current horizontally. For the vertical hydrogen flame a special copper tip was used on the blow-pipe. This gave a flame about 2 to 3 cm in diameter and from 1 to 20 cm in length as desired. The bore of the copper tip was about 3 mm in diameter at the outlet and 4 mm at the intake end. This conical bore prevented backfiring and steadied the flame. Two horizontal burners were made, one for gasoline vapor and one for hydrogen. These burners differ from previous types in that the number of quartz tubes used per unit length was increased by using tubing of a small diameter; thus the cones in the flame were small and close together. For the gasoline burner, 17 quartz tubes, each 2.5 cm long and having an inside diameter of 2.5 mm, were mounted on a brass tube of about 1.5 cm inside diameter. The centers of the tubes were placed about 0.5 cm apart, thus making the burner about 8.5 cm long.

This burner could not be used for hydrogen, for the addition of a small amount of air would cause the flame to blow back and burn inside. It was found however by taking small quartz tubing of about 3 mm inside diameter and heating one end in an oxy-hydrogen flame until it contracted to a diameter of about 2 mm, that considerable air could be added to the hydrogen flame before it blew back inside the burner. The horizontal burner was not so easy to control as the vertical blow-pipe, so that most of the work with hydrogen was done using the blow-pipe.

Gouy sprayers were used to mix various salts with the air. In the case of chloroform, carbon tetrachloride, and bromine, a double air path was used. By means of pinch-cocks the air could be made to pass over the liquid carrying the vapor with it, or by the other path air alone entered the burner.

The hydrogen and chlorine were obtained in the usual commercial tanks, and by suitable pressure regulators, any desired amount of each could be admitted to the flame. A motor driven blower, acting through a pipe line opening over the flame, was used to pump the HCl gas outdoors. Even then it was necessary to wear a gas mask while working with the hydrogen-chlorine flame.

The electrodes consisted of platinum wire, with small cross wires on the end. The negative electrode was kept coated with sealing wax and

the resulting oxides served to reduce the negative fall of potential and produce a uniform gradient in the flame. The potential difference was applied by means of a 300 volt battery connected in series with a galvanometer. The Hall effect angle was measured by means of two platinum probes mounted on the ends of two copper wires which were insulated from each other and supported by two coaxial quartz tubes. This probe assembly extended into the flame through a hole drilled in one of the pole-pieces of the magnet. The copper leads on the outside were connected to an electrometer having a sensitivity of about 5 cm per volt. The galvanometer and electrometer circuits were kept entirely insulated from the ground.

There is no simple method by which the absolute temperature of a flame can be quickly determined, and since relative values serve almost as well in the present case, a platinum-platinum-rhodium thermocouple was adopted. This thermocouple was placed near one of the electrodes in such a position as not to affect the current. In a well oxidized blue gasoline flame the couple gave a temperature of 1200°C. The actual temperature<sup>9</sup> of such a flame is about 1870°C. In all cases the temperature as given by the couple has been used in this paper. The thermocouple was very useful in maintaining constant flame conditions. Flames of the same character at a given temperature could be consistently reproduced from day to day.

#### THEORY

The mobility of the positive and negative ions in a horizontal flame may be expressed by the following formula;<sup>10</sup>  $k_1 - k_2 = (1 - dR/R) Y/XH$ , where  $k_1$  = mobility of positive ions,  $k_2$  = mobility of negative ions,  $X$  = horizontal electric field,  $Y$  = vertical electric field due to the Hall effect,  $H$  = magnetic field, and  $dR/R$  = magneto-resistance effect, or fractional increase of resistance of the flame when the magnetic field is on.

Since  $k_1$  is small compared with  $k_2$ , and  $Y/X = \tan \theta$ , where  $\theta$  is the angle through which the probes must be rotated to bring the electrometer deflection back to zero when the magnetic field is on, the formula becomes, neglecting the resistance term,  $k_2 = -10^8 \tan \theta / H$  cm/sec. per volt per cm. In all measurements of the angle  $\theta$ , the necessary data for computing the potential gradient and the temperature were recorded at the same time. The magneto-resistance term  $dR/R$  was omitted in the formula, for the correction amounted to not more than 4 percent about the magnitude of the experimental error.

<sup>9</sup> Hodgman and Lange, *Handbook of Chemistry and Physics*, p. 526.

<sup>10</sup> C. W. Heaps, *Phys. Rev.* **24**, 652 (1924).

The simple type of theory indicates that the mobility of negative ions in a gas should vary with the square root of the absolute temperature if the mass remains constant. By varying the temperature it was thought that some confirmation of this conclusion might be found. The data, however, do not agree with this theory, hence there must be other factors entering which the simple type of theory does not contemplate. It seems probable that the mass of the ion is a function of the temperature. Above the flame where the temperature was 475°C, Saxer<sup>11</sup> found the mobility

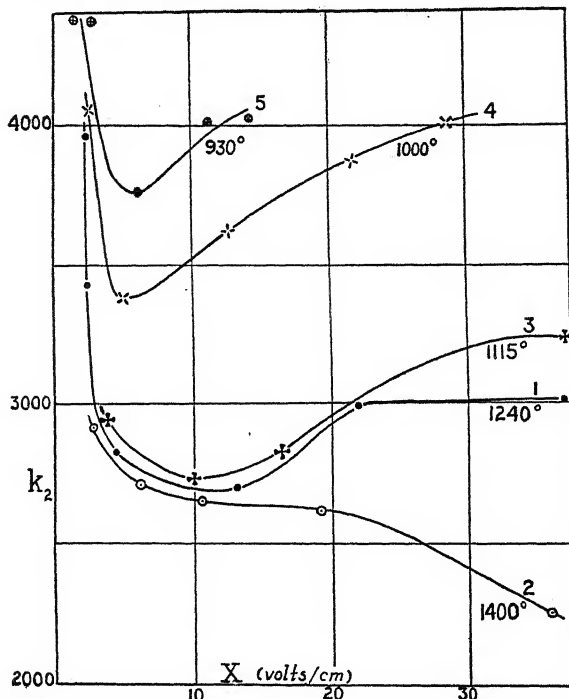


Fig. 1. Mobility of negative ions in the horizontal gasoline flame as a function of potential gradient for various flame temperatures.

of the negative ions to be only 4.39, a value comparable with that of the positive ions. In the hot part of the flame the mobility may be several thousand, so it appears that high temperatures may tend to break up cluster ions, decreasing their average mass and thus increasing  $k_2$ .

#### EXPERIMENTAL RESULTS

A. *Temperature variation.* By the addition of air and oxygen the temperature of the gasoline and hydrogen flames was varied and measurements of the mobility and potential gradient made. Fig. 1 shows graph-

<sup>11</sup> A. H. Saxer, Phys. Rev. 3, 325 (1914).

ically the effect of varying the temperature of the horizontal gasoline flame. Each curve represents measurements taken at a constant temperature. Curve 1 was obtained with a well oxidized blue flame, the temperature of the thermocouple being 1240°C. Oxygen was added to raise the temperature to 1400°C and data for Curve 2 were taken. The mobility for large gradients decreased. The Curves 3, 4, and 5 at the lower temperatures, were obtained by reducing the air supply. The upper part of the flame for these curves was luminous, though the electrodes were kept in the blue part of the flame. If the electrodes are placed in the luminous part, carbon collects rapidly on the electrodes and measurements are not reliable. For large gradients it will be noted that the mobility was varied from 2300 to 4000 by adding various amounts of air and oxygen.

In the horizontal hydrogen flame the mobility varied from 3500 to 2600 for a variation of potential gradient from 3 to 20 volts per cm. The temperature could not be changed much, and  $k_2$  was practically constant for the temperatures used. Two sets of data chosen at random from that taken with the vertical hydrogen flame are given in Table I.

TABLE I  
*Typical results for vertical hydrogen flame*

Temp.	Battery e.m.f. (volts)	Current ( $10^{-8}$ amp.)	$X$ (volts/cm)	$k_2$
1215°C	20	24	4.1	4170
	40	44	9.3	4310
	80	75	20.4	4600
	130	90	32.2	3420
	170	110	44.1	3900
1370	20	30	4.2	4170
	40	59	8.8	4120
	80	105	19.5	4520
	130	170	33.8	5340
	170	190	42.2	5100

For low values of  $X$  the value of  $k_2$  is about the same for both temperatures, but for large gradients the value of  $k_2$  is larger at the higher temperature. All data taken show the same variation, so that the mobility for large gradients in the hydrogen flame undoubtedly increases with temperature.

B. *The effect of chloroform and carbon tetrachloride.* A two way air path was connected so that when desired the air furnished to the vertical hydrogen flame could be made to pass over liquid chloroform. A constant voltage of 80 was applied to the flame, the electrodes being one above the other, and the mobility was measured for various proportions of hydrogen,

air, and chloroform. At a thermocouple temperature of 1410°C (the electrodes were near the melting point and the hydrogen flame was probably around 2000°C), the value of  $k_2$  for the free flame was 4800. Then as the chloroform path was opened,  $k_2$  dropped to 4380, and finally with all the air passing over chloroform,  $k_2$  was 3250. Then on lowering the temperature from 1410°C to 1190°C, by reducing the amount of hydrogen, leaving air and chloroform the same,  $k_2$  dropped to 1625. The Hall effect angle for other potential gradients, with the air passing over liquid chloroform, varied from 3.2° to 4.8°, corresponding to values of  $k_2$  ranging from 1230 to 1875.

The effect of the chloroform on the gasoline flame was even more striking, for here the Hall effect angle of 10.5° for the free blue flame dropped to 1.1° for a magnetic field of 5000 gauss. These angles correspond to a change of  $k_2$  from 3690 to 384.

Another compound of chlorine, carbon tetrachloride, was mixed with the air-hydrogen flame. Table II shows the effect of varying the temperature of the flame while the amount of  $\text{CCl}_4$  added remained constant.

TABLE II  
*Results for air-hydrogen flame with  $\text{CCl}_4$  added*

Temp.	$X$ (volts/cm)	Angle	$H$ (gauss)	$k_2$
1180°C	2.48	2.85°	4500	1110
	9.85	2.85	4500	1110
	20.6	3.3	4480	1285
	39.0	3.75	4500	1450
	46.0	4.15	4500	1610
1350	2.35	5.35	4480	2090
	8.7	6.35	4480	2490
	17.3	7.2	4400	2870
	35.0	9.1	4400	3640
1180	45.0	4.55	4400	1800

The temperature was varied by adjusting the hydrogen needle valve, the amount of air and  $\text{CCl}_4$  remaining approximately constant. By changing the temperature of the thermocouple from 1180°C to 1350°C the mobility of the negative ion was practically doubled. When the temperature was again reduced to 1180°C  $k_2$  dropped to 1800, a somewhat higher value than in the first instance. The lack of agreement is probably due to the rate of introduction of  $\text{CCl}_4$  decreasing with time.

Hydrochloric acid gas is formed in the flame by the breaking up of chloroform and carbon tetrachloride. Any salt or oxide coating placed on the electrodes is removed in the flame in a few minutes. The electrodes



are so well cleaned that when subsequently used in the free hydrogen flame, with considerable applied potential, the current is so small that measurements of the gradient and Hall effect angle cannot be made. Most of the potential drop occurs very near the cathode if the latter is free of lime or salts.

C. *The effect of iodine and bromine.* Since compounds of chlorine cause such marked decreases in  $k_2$  in the flame, it was thought that iodine and bromine, being also electronegative and having other properties similar to chlorine, might decrease  $k_2$ . Iodine exists in a crystalline form at ordinary temperatures and is therefore more difficult to add to the flame, than chloroform. The data for Table III were obtained by first spraying alcohol into the flame, and then a solution of iodine crystals in alcohol.

TABLE III

*Results for hydrogen flame when alcohol and solution of iodine in alcohol is added*

Spray	Temp.	Battery e.m.f. (volts)	Current ( $10^{-7}$ amp.)	$X$ (volts/cm)	$k_2$
Alcohol	1330°C	20	40	5.1	4580
		40	101	9.7	4880
		100	175	24.6	4550
		190	200	46.0	5360
		275	250	75.0	5690
Alcohol and iodine	1340	20	20	4.9	3810
		40	57	9.1	4660
		100	72	22.6	4380
		190	83	69.7	4680
		275	130	82.0	4000

With the addition of the iodine to the alcohol the current for the same applied voltage was decreased to one half and  $k_2$  shows a definite decrease for all values of potential gradient. The quantity of iodine added to the flame in this experiment was probably small compared with the amount of chloroform added in the previous experiment. It is possible that larger proportions of iodine to air would cause a decrease in  $k_2$  comparable with that produced by chloroform.

Liquid bromine was placed in one air path and added to the hydrogen flame. Bromine boils at 58.7°C and being quite volatile its vapor mixed readily with the passing air. The flame became bluish in color with a faint trace of yellow, and the oxide coat on the cathode disappeared as a deep red vapor. The Hall effect angle decreased from 10° to less than 1° for a field of 4800 gauss, which is the largest decrease in angle produced by any of the substances except chlorine gas. The corresponding decrease in  $k_2$  is from 3700 to 360.

D. *The effect of NaCl, Na<sub>2</sub>CO<sub>3</sub>, NH<sub>4</sub>Cl, and KCl.* The effect on  $k_2$  produced by the addition of the chlorine compounds already described made it seem worth while to test other compounds of chlorine. For this purpose normal solutions of sodium chloride and sodium carbonate were sprayed into the hydrogen flame under the same conditions and compared. Table IV shows some of the data obtained at constant temperature.

TABLE IV

*Results for hydrogen flame into which normal solutions of NaCl and Na<sub>2</sub>CO<sub>3</sub> are sprayed*

Salt	Temp.	X (volts/cm)	Angle	$k_2$
NaCl	1290°C	2.1	14.9°	5610
		2.9	13.9	5180
		5.1	13.9	5330
		10.1	13.5	5210
Na <sub>2</sub> CO <sub>3</sub>	1290°	2.2	13.3	5190
		3.4	13.6	5200
		7.2	13.8	5400
		10.1	13.6	5380

The values of  $k_2$  for NaCl and Na<sub>2</sub>CO<sub>3</sub> in the hydrogen flame are practically the same.<sup>12</sup> Thus Cl introduced in the form of NaCl has no more effect on the mobility than CO<sub>3</sub> introduced as Na<sub>2</sub>CO<sub>3</sub>. The above data show that the value of  $k_2$  for the salted vertical hydrogen flame is about 20 percent higher than for the free hydrogen flame at the same temperature.

A normal solution of potassium chloride sprayed into the hydrogen flame gave a mobility practically the same as was obtained with sodium chloride.

A concentrated solution of ammonium chloride was sprayed into the flame. The oxide coated cathode gave off a red vapor just as when chloroform was added. No doubt considerable HCl was formed in the flame since NH<sub>4</sub>Cl dissociates into ammonia and hydrochloric acid at a temperature of 337.8°C. Values of  $k_2$  were obtained varying from 3400 to 1770. The NH<sub>4</sub>Cl thus produces a diminution of mobility which is quite appreciable.

E. *Distilled water and NaCl solution in the gasoline flame.* Some measurements were made on the gasoline flame, first spraying distilled water and then a solution of NaCl into the flame. The results for the small quartz tube burner were similar to those obtained by Watt,<sup>3</sup> who

<sup>12</sup> H. A. Wilson has reached this same conclusion in the case of a gasoline vapor flame, loc. cit.<sup>2</sup>

used a large burner, large electrodes, and a larger current. The value of  $k_2$  varied from about 3000 to 2000 and decreased with the increase in potential gradient, as he found to be the case. Contrary to his results,  $k_2$  for small gradients at least was slightly higher for the salted flame than for the one containing distilled water. This behavior is similar to that in the case of the hydrogen flame, where  $k_2$  is higher for the salted than for the free flame.

F. *The effect of chlorine gas using the hydrogen flame.* At ordinary pressures and temperatures chlorine may be fed directly to the hydrogen flame, using the blow-pipe, without air being added. The hydrogen-chlorine flame is characterized by a blue greenish color and a high temperature, equal to that of the air-hydrogen flame. Any salts on the electrodes are rapidly removed. The current through the flame was of the same order as that in an air-hydrogen flame with the cathode coated with oxides. The electrometer reading was much steadier than in the air-hydrogen flame.

Other writers working with the hydrogen-chlorine flame, have concluded that the positive ions have a greater mobility than the negative ions. The theory of the Hall effect indicates that if the mobility  $k_1$  of the positive ions equals  $k_2$  for the negative ions, the Hall effect will be zero, and if the positive ions have a greater mobility than the negative ions, the Hall effect changes sign.

Chlorine was added until the temperature of the flame was almost sufficient to melt the electrodes, but in no case could a reversal in the Hall effect angle be detected. Samples of values obtained for the angle and for  $k_2$  are shown in Table V.

TABLE V

*Results for hydrogen-chlorine flame*

Angle	$H$	$k_2$
1.65°	5000 gauss	576
0.15	4975	52
0.6	4975	210
0.25	4650	94
0.3	4650	113
0.25	4650	94
0.2	4650	70

The smallest angle measured was 0.15°. Although the experiments were repeated on several days, there was no doubt about the direction of rotation of the Hall effect angle; it always indicated a greater mobility of the negative than of the positive ion.

Next some measurements were made on the potential gradient at different parts of the flame. Kalendyk<sup>8</sup> found a larger potential gradient at the anode than at the cathode for the hydrogen-chlorine flame.

The flame and the current electrodes were arranged so that they could be moved vertically, the potential probes being fixed through the pole-pieces of the magnet. In all trials the potential gradient was found to be greater at the anode, which was the lower electrode. But a large drop of potential at the anode indicates that the positive ions have a greater velocity than the negative ions. By the Hall effect method, however,  $k_2$  was always greater than  $k_1$ . Then it was thought that the velocity of the flame gases might have some influence on the potential drop, so the potential gradient was measured with the upper electrode as the anode. Again a much larger drop in potential was found near the lower electrode, now the cathode. These tests were repeated several times on different days and always agreed. The conclusion to be drawn is that  $k_2$  is greater than  $k_1$  in the hydrogen-chlorine flame but that the actual velocity of the positive ions may be greater than that of the negative ions. The velocity of the flame gases is an important factor to consider. For a quartz tube burner the velocity is about 200 cm per sec. The velocity for the blow-pipe burner used was certainly very much greater than this, so that when plenty of chlorine is used in the flame the velocity given to the negative ions by the flame motion is greater than the velocity given by the electric field, unless the latter is quite large.

The large potential drop at the lower electrode no matter whether it is made the anode or cathode is therefore explained as follows. If the lower electrode is the anode then the positive ions are carried up both by the flame and by the electric field while the negative ions must move down against the flame motion. Thus the positive ions have their velocity increased and the negative ions have theirs decreased, the resultant velocity of the positive ions is greater than that of the negative ions, and a negative space charge is set up around the anode. The anode fall of potential is in this case greater than the cathode fall. The Hall effect angle indicates that under these conditions the mobility of the negative ions is not much greater than that of the positive ions.

If the upper electrode is now made the anode, the positive ions must move down against the flame motion and the negative carriers will move up with the flame gases. Thus the negative ions have a greater velocity than the positive ions, which in this case are retarded by the gas motion. This condition results in a larger potential drop at the cathode than at the anode.

The effect of chlorine on the gasoline flame is similar to that of chloroform. If no air is mixed with the gasoline vapor the flame becomes luminous. On adding chlorine gas, the flame remains luminous,  $k_2$  is small, and measurements are difficult since carbon collects rapidly on the electrodes.

#### CONCLUSIONS

The effect of flame temperature on the mobility of the negative ion cannot be predicted by the simple formula of kinetic theory. As the temperature of a gasoline vapor flame is raised by the addition of oxygen the mobility of the ion decreases. If hydrogen is burned instead of gasoline vapor the mobility increases with temperature, at least in a strong electric field. It appears probable that the negative ion during its life is a free electron part of the time and a charged atom or cluster of atoms the rest of the time. The mobility will diminish as the fraction of the ion's life as a free electron diminishes. A high temperature should be unfavorable to the existence of ionic clusters, so one would expect the mobility to increase with temperature. However, to increase a flame temperature the character of the flame must be changed and possibly constituents appear which have a tendency to attach the free electrons. In this way the diminution of mobility of the negative ion in the gasoline flame may be explained.

The experiments show clearly that feeding Cl, Br, and I into a flame diminishes the mobility of the negative ion. Franck and Pringsheim maintain that in a hydrogen-chlorine flame the negative ion is practically never a free electron. The present experiments indicate that Br and I behave like Cl in the hydrogen flame, and that the electron is quickly attached to atoms of the introduced halogen, or possibly to combinations of the halogen with hydrogen. When the temperature of the  $H_2$ -air- $CCl_4$  flame was raised by varying only the  $H_2$  constituent the mobility of the negative ion increased. In this case the higher temperature evidently tended to prevent the attachment of Cl or of HCl to the electron.

If Cl is fed into the flame as NaCl or KCl it does not appear to slow up the negative ion. However, when introduced as  $NH_4Cl$ ,  $CCl_4$ , or  $CHCl_3$  its effect is decidedly evident. The latter compounds are easily broken up so that a Cl or possibly HCl molecule is free to attach an electron. The breaking up of the salts of the metals does not appear to be extensive enough to produce constituents which can attach electrons, or possibly an electron is produced for each atom of metallic salt which is broken up. In the latter case the negative ions would be a mixture of free electrons and ionic clusters.

These experiments do not corroborate the conclusion of Franck and Pringsheim that the mobility of the negative ion in the hydrogen-chlorine flame is less than that of the positive ion. The presence of a potential drop at the anode larger than that at the cathode may be caused by the high velocity of the flame gases, even though the mobility of the negative ion is greater than that of the positive ion.

I wish to express my thanks to Dr. C. W. Heaps for his unfailing interest and helpful suggestions in carrying out this investigation. I am also indebted to Dr. H. A. Wilson for making the arrangements by which I could carry on the work.

PHYSICAL LABORATORY,  
THE RICE INSTITUTE,  
July 8, 1925.

# MEASUREMENT OF THE FOUR MAGNETIC TRANSVERSE EFFECTS

By EDWIN H. HALL

## ABSTRACT

This paper presents in detail the experimental arrangements and technique used by the author in measuring the four magnetic transverse effects (the Hall, Ettingshausen, Nernst and Leduc effects) on the same strip of metal, in succession. The strip 5 cm long by 2 cm wide by .01 to .06 cm thick depending on the metal, is soldered to two brass end blocks which may be independently cooled or heated with water or steam. The pole pieces, 4.5 cm in diameter and 0.7 cm apart, are thermally insulated from the strip by flannel and mica. The temperature of these pole pieces is adjusted to approximately that of the middle of the strip, by water cooling or heating. Ten thermo-junctions are soldered at various points along one edge and along the median line of the strip and one at the middle of the other edge. These enable longitudinal and transverse potential and temperature gradients to be measured. Various corrections are discussed, including (a) effect of size of thermo-junctions, (b) the effect of the limited length of the strip with reference to the width, (c) masking influence of one transverse effect on another, (d) effects of non-uniformity of temperature gradients due to heat leakage to or from the strip. Also certain precautions in the measurement of the separate effects are given. Results for Au, Pd, Ni, Co, previously published in summary are here given with some details, including corrected values for the *Ettingshausen effect for palladium*.

I PROPOSE to exhibit in this paper the methods and devices which I have used in recent experimental work<sup>1</sup> upon the four "transverse" effects of the magnetic field, the definitions and sign conventions of which are illustrated by Figs. 1-4.

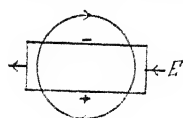


Fig. 1  
Hall effect,  
 $R$  or  $eT_e$   
positive.

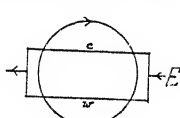


Fig. 2  
Ettingshausen effect,  
 $P$  or  $eT_h$   
positive.

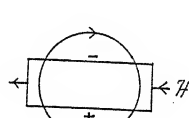


Fig. 3  
Nernst effect  
 $Q$  or  $hT_e$   
positive.

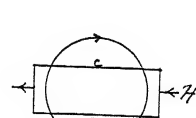


Fig. 4  
Leduc effect,  
 $S$  or  $hT_h$   
positive.

## APPARATUS

The pole pieces of my magnet are about 4.5 cm wide, and I usually have them 0.7 cm apart. The strip or plate of metal to be studied is commonly about 5 cm long and 2 cm wide, and it is mounted in such a

<sup>1</sup> E. H. Hall, Proc. Nat. Acad. Sci. 11, p. 416 (July 1925).



way that, barring accidents, it need not be removed from its position between the poles, or even be disturbed there, during the measurement of all four effects at various temperatures. Thus, in Fig. 5, the scale of which is half full size,  $WW$  is a board (a small drawing-board, 9 inches wide, is suitable) in which a hole is bored just large enough to admit the magnet pole  $P$ ; it is backed by a wooden boss of such thickness as to bring the outer surface of the board a little beyond the face of the pole; it carries two brass blocks  $BB$  bolted to it, and to the thinned opposed ends of these blocks the ends of the experimental metal strip  $m$  are soldered. The distance of  $m$  from the pole  $P$  is about 0.25 cm and from the pole  $P'$  somewhat greater, this greater distance allowing room for

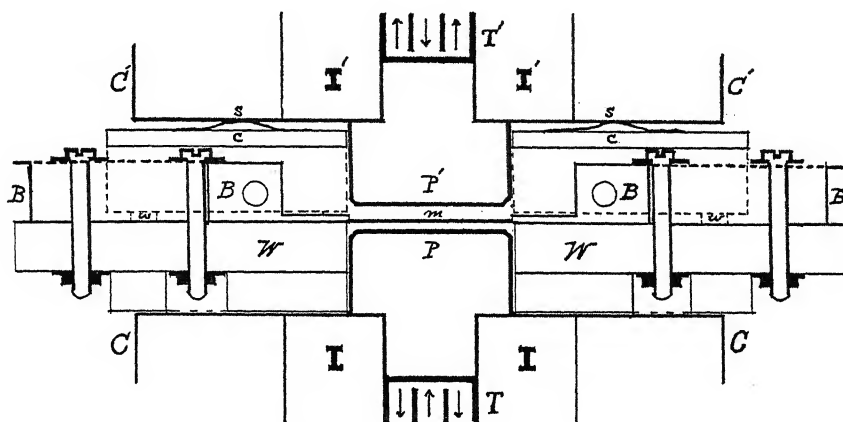


Fig. 5. The experimental plate  $m$ , and the method of mounting between the poles of the electromagnet, all as seen from above.

the somewhat elaborate wire connections indicated in Fig. 6. A wooden cover  $cc$ , channeled in such a way as to bridge over the blocks  $BB$ , is fastened by screws, not shown, to the board  $WW$ ,  $ww$  being washers of such thickness as to prevent pressure on the tops of the bolts passing through  $BB$ . Springs, indicated or suggested by  $ss$ , pressing against the face of the coil  $C'C'$ , hold the rear surface of the wooden boss, behind  $WW$ , against the face of the coil  $CC$ , thus fixing the position of  $m$  between the poles. Everything shown between the face of  $CC$  and the face of  $C'C'$  can be handled as one coherent *ensemble*. Before measurements begin, crevices leading into this *ensemble* or existing between it and the faces of the coils are stuffed with cotton, to reduce currents of air, which otherwise are likely to make trouble when a considerable difference of temperature exists between the interior and the exterior.

Fig. 6, which is also half full size, shows one corner of the board *WW* and the things it carries. The right-hand block *B* is channeled, and its channel leads into a short horizontal brass tube connecting with a larger vertical one, to which is attached, by means of the coupling *K*, a stuffing-box *S* carrying a thermometer *t*. Water, entering through a tube at *T*, circulates through the channel of *B* and escapes at *T'*, just above the bulb of the thermometer. When steam instead of water is used, it enters at *T'* and comes out at *T*. *G* is a brass guide piece intended to maintain

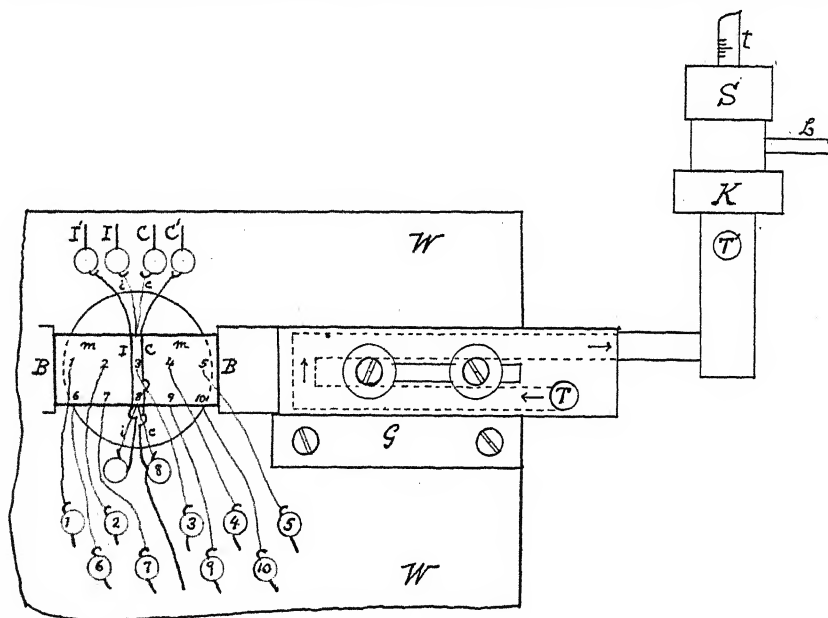


Fig. 6. *WW* is one corner of the board carrying the experimental plate *mm* and its attachments. The circle behind *mm* represents one pole of the electromagnet.

the proper alignment of *B* when the bolts fastening the latter to the board are loosened. The other block *B*, the end only of which is shown in Fig. 6, is, with its connections, a left-hand counterpart of the right-hand block.

When one of the electromagnetic effects, the Hall or the Ettingshausen, is to be measured, streams of the same temperature are sent through both channels so as to give both of the blocks *B*, and thus both ends of the metal strip *mm* connecting them, the same temperature. Then an electric current is led in or led out by the wire *L* and a corresponding wire at the other end of the apparatus. Of course, the mid-length part of *mm* will not necessarily have the same temperature as the ends. The whole matter of the temperature control of the middle part will be discussed at length farther on.

When one of the thermo-magnetic effects, the Nernst or the Righi-Leduc, is to be measured, electric connection is broken at each  $L$  and streams of different temperature, one being sometimes a flow of steam, are sent through the two channels, thus producing a temperature gradient along the plate  $mm$ .

At point 8, mid-point of the lower edge of the plate  $mm$ , a thermo-electric junction, of No. 40 copper wire and No. 40 "ideal" wire twisted together, is soldered. A similar couple is attached in the same way at the mid-point of the upper edge of  $mm$ . Much care should be taken with these junctions. They should be small, compact, firm, and firmly attached to the plate, with no superfluity of solder. A method of making them is indicated in Fig. 7.  $A$  is a fixed bar carrying two screws 16 cm apart, beneath the heads of which the fine wires, one of copper, the other of "ideal," are fastened.  $B$  is a movable bar about 8 cm from  $A$ . As shown

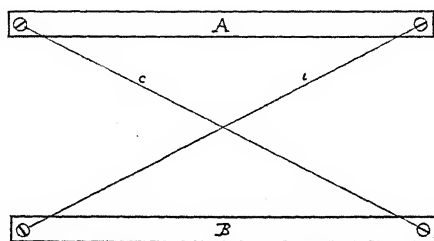


Fig. 7



Fig. 8

Fig. 7. Illustrating the method of making the thermo-electric junctions.

in the figure the two wires are merely crossing each other in contact. Bar  $B$  is now turned, in a vertical plane, through a complete revolution and thus reaches its original position, a gentle tension on the wires being all the time maintained. Each wire is thus twisted once completely around the other in a close spiral about 0.5 mm long. This junction is now soldered, the wires having been cleaned before twisting. Then with a sharp knife the wires on one side, say the side toward  $B$ , are cut off close to the junction, which is thus ready to be soldered to the plate. (See "8" in Fig. 8, corresponding to the point marked in the same way in Fig. 6.) The two opposite junctions, each extending about 0.5 mm on the plate 2 cm wide, reduce its effective width to an extent not easy to determine with precision, but the maximum must be less than 5 percent. I suggest that a correction, to be called *correction (a)*, be added to each of the observed transverse differences of potential or of temperature, this correction being such a percentage of the observed value as the length of *one* junction is to the width of the plate.

If a junction does not have very good and close attachment to the plate, we can not be sure that its changes of temperature follow satisfactorily those of the plate at the point of attachment. In fact, under the best practicable conditions the temperature of a junction cannot be controlled solely by that of the plate, as the packing material, and the fine wires leading away from the junction, must have some influence. This condition tends to make the observed transverse temperature differences, from which the Ettingshausen and the Righi-Leduc coefficients are estimated, somewhat less than the real differences existing in the plate.

The wires indicated in Fig. 8 should be so arranged as to make the circuits into which they enter as nearly non-inductive as may be, for changes of intensity of the magnetic field. Otherwise, a slight change of strength of the magnetizing current, say 1 percent, occurring suddenly by reason of an imperfect connection, may produce a very disturbing deflection of the galvanometer needle.

The copper wires only of these two junctions are used when transverse potential differences, the Hall and the Nernst effects, are to be measured. More will be said farther on concerning the thermo-electric use of the junctions.

The other wires shown in Fig. 6 as attached to the plate *mm* are for the purpose of measuring the longitudinal temperature differences along two lines of the plate, the median line and the lower boundary line. These wires should not be larger than No. 40, about .08 mm in diam., and must be of such material as to give effective thermo-electric couples with the material of the plate. Thus, if the latter is of nickel, palladium, cobalt, etc., the wires should be of copper. If the plate is of copper, or of gold or silver, these wires may be of constantan ("ideal"). The points of attachment of the wires are intended to be 1 cm apart, but since accurate placing is difficult, measurements of distances are made after the soldering, and these actual distances are used in calculating temperature gradients. At no great distance from the plate *mm* each of the fine wires attached to it is soldered to a thicker wire of the same material to lessen electrical resistance and the danger of breaking.

*Calibration of thermo-electric couples.* On the advice of Mr. W. P. White of the Carnegie Geophysical Laboratory, I use the soft, "ideal," constantan wire that is produced by the Electrical Alloy Company of Morristown, N. J. My own calibration tests of couples made of No. 40 "ideal" and No. 40 copper wire show, all the way from 0°C to 85°C, sensitivity values about 6 percent greater than those given in the tables of Mr. L. H. Adams for copper-constantan couples. Couples made of copper

and the coarser "ideal" wire mentioned above were about 3 percent less sensitive than those having the fine wire. I did not attempt to allow for this difference in using, as described above, circuits in which coarse wires were joined to fine wires, but took the values given by the fine wire couples as holding in my measurements of the transverse effects.

I made a special test for any effect of the magnetic field, about 9000 gauss, on the sensitiveness of a copper-ideal couple, both junctions of which, besides the whole length of the constantan wire, were between the poles. The effect of the field, if there was any effect, was only a small fraction of one percent of the total power of the couple.

For couples in which constantan was not one of the metals, I made no calibration tests but calculated the thermo-electric powers from data given by Bridgman in his paper<sup>2</sup> on "Thermo-electric Qualities Under Pressure."

*The question of strip dimensions; correction (b).* The best length and width of the metal strip to be used will naturally depend on the width of the magnetic field that can be regarded as fairly uniform. With pole pieces 4.5 cm in diameter I use, as has been said above, a strip about 2 cm wide and 5 cm long, between lines of attachment to the blocks *B* and *B*. Considerable width is desirable, in order to reduce the importance of the encroachment of the junctions upon the plate, as in Fig. 8; but, on the other hand, great width tends to increase the short-circuiting influence of the ends which lie outside the intense magnetic field, and of the blocks *BB*, to which these ends are fastened. This short-circuiting, which doubtless occurs with all four of the transverse effects and is probably about equally great, relatively, for all of them, was observed in 1886 by Ettingshausen and Nernst<sup>3</sup> working with a plate of bismuth and by myself<sup>3</sup> in 1888 working with a plate of soft steel, in experiments showing that the Hall effect is, other things being equal, notably smaller in a short strip of metal than in a long strip. I have recently made more careful and extended observations for the purpose of determining, approximately, what percentage of correction should be made for the error due to the fact that the strip I use is of limited length. I studied the Hall effect in a thin gold strip of variable effective length.

Fig. 9 illustrates the apparatus used. *WW* is, as before, a flat board, with a hole to receive the pole piece *P*. A thin glass plate *gg* is sunk into a depression in this board and on this plate rests a gold strip *m*, 2 cm wide, 5.1 cm long and about 0.013 cm thick. Semi-cylindrical blocks of

<sup>2</sup> Bridgman, Proc. Amer. Acad. 53, 269-386.

<sup>3</sup> See Campbell, "Galvanomagnetic and Thermomagnetic Effects" (Longmans), pp. 31 and 32.

brass, *cc*, somewhat longer than the width of the gold, rest on *m* and are pressed firmly against it by the stiff springs *ss*. The distance between these blocks, beginning with 0.5 cm as shown in Fig. 9, could be increased by convenient stages till it equalled almost the whole length of the strip. It is assumed that the Hall effect in the thick movable blocks is negligible

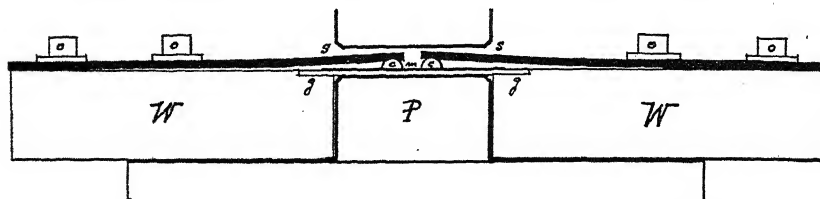


Fig. 9. This shows, as seen from above, the device used for varying the effective length of the experimental strip.

and that the gold immediately under and in contact with a block can be treated as a part of the block. The values of the Hall coefficient *R* found are given in Table I.

TABLE I  
*Variation of Hall coefficient with the effective length  $x$  of the strip*

$x$	$R(\text{obs.})$	$R(\text{calc.})$	Contribution to $R$ of	
0.5 cm	-0.000500	-0.000531	1st 0.5 cm	-0.000531
1.0	-0.000594	-0.000593	2nd "	-0.000062
1.5	-0.000622	-0.000627	3d "	-0.000034
2.0	-0.000646	-0.000649	4th "	-0.000022
2.5	-0.000669	-0.000665	5th "	-0.000016
3.0	-0.000683	-0.000678	6th "	-0.000013
3.5	-0.000688*	-0.000688	7th "	-0.000010
4.0	-0.000695	-0.000695	8th "	-0.000007
4.8	-0.000705	-0.000705	9th (0.8 cm)	-0.000010

\* This is the mean of two values 691 and 685 obtained several days apart.

Representing by  $x$  the variable block-distance in centimeters, I found by an empirical process the following formula, which corresponds fairly well with the observations.

$$R = -0.00077(1 - 0.23x^{1/2}). \quad (1)$$

It must be noted that the distance  $x$  was not very accurately measured and that any given error in the value of  $x$  will have its greatest effect when this distance is small. The values calculated with this formula are also given in Table I.

Of course formula (1) indicates that with an infinite value of  $x$ , in a magnetic field of uniform strength, the maximum value of  $R$  would be  $-0.000770$ . As the value of  $x$  is about 5 cm in my ordinary experiments, Table I, which gives  $R = -0.000705$  for  $x = 4.8$  cm, indicates that I



should add about 8 percent to my ordinarily observed values of  $R$  in order to make due correction for the limited length of the metal strip used. This is for a strip 2 cm wide. The correction to be applied increases with the width of the strip.

As this correction is due to the short-circuiting effect of transverse conduction around the ends, and as such conduction should have about the same proportional effect in the case of transverse thermal difference as in the case of transverse potential difference, I assume that to every transverse gradient *actually existing* at mid-length of a strip 5 cm long and 2 cm wide, an addition of 8 percent should be made, to take proper account of this short-circuiting influence. This correction, then, *which hereinafter will be called correction (b)*, applies to all four of the transverse effects. In some cases, where other corrections to be applied are large, it is a matter for consideration whether this 8 percent shall be added before or after other corrections. The words "actually existing," which I have italicized, are decisive in this connection.

There is, however, another way of looking at this matter, a way which I find useful in another connection, as will presently appear. This is to think of the middle half-centimeter of the strip as contributing a certain amount to the transverse gradient, whether electrical or thermal, which is found there, and of each successive element of the length of the strip, toward either end, as contributing also its share, these contributions, for a given increment of length, decreasing as distance from the middle increases. The last column of Table I was made in accordance with this view from the values given under  $R$  (calc.).

*Thermo-electric complication in measurement of transverse potential difference; correction (c).* If in the measurement of a transverse potential (Hall effect or Nernst effect), the side-connection wires used are not of the same metal as the strip  $m$ , these wires, together with the part of  $m$  which connects them, constitute a thermo-electric couple which, because of the difference of temperature of its two junctions (Ettingshausen effect or Righi-Leduc effect), tends to make the Hall effect or the Nernst effect appear either greater or less than it should be. Correction of the observed transverse potential difference must be made accordingly, and so the Ettingshausen effect must be measured before the final value of the Hall effect can be known, and the Righi-Leduc effect before the final value of the Nernst effect can be known.

This correction, *which will be called correction (c)*, may be very large. Thus in one case, with copper wires leading from a cobalt strip, the final value of the Nernst coefficient  $Q$  was about 70 percent of the value found without this correction.



*Longitudinal temperature gradient; corrections (d) and (e).* The temperature conditions of the strip  $m$  are difficult to control satisfactorily. Through a packing of cotton flannel and mica disks there is a notable flow of heat between the strip and the neighboring pole-faces, unless the latter are in some way brought nearly to the same temperature as the strip itself. Unwin<sup>4</sup> interposed between  $m$  and the poles a thin metal channel through which water of any desired temperature flowed, and I have tried a similar device, but on the whole I do not like it. Unless one makes the distance between the pole pieces greater than the distance I have used, 0.7 cm, he must make the water channel so thin that it is likely to become obstructed by bubbles when hot water is used.

In my more recent experiments I have endeavored to keep the temperature of the pole pieces as nearly as possible the same as that of the middle of the strip  $m$ . For this purpose I have sent through the double brass tubes  $T$  and  $T'$  (Fig. 5), which fit into the bore of the magnet cores, water of suitable temperature. But this device, used alone, operates rather slowly, and I am planning to use magnet coils the windings of which will consist of copper tubing carrying a stream of water, cold or hot according to the pole temperature desired. A thermo-electric couple, one junction of which presses against the side of a pole piece, enables me to keep watch of its temperature changes.

It is evident from what has been said that a uniform temperature gradient cannot be maintained from one end to the other of the strip  $m$ . If the pole pieces have the same temperature as the mid-length of the strip, the warmer end of the strip will lose heat to the poles and the cooler end will gain heat from the poles, the result being that the longitudinal temperature gradient of the strip will be flattened in the middle but steeper at each end, the general shape being that shown by the curve in Fig. 10. This is a line of double curvature, the point of change from concave to convex being near the middle of the strip, in fact just at the middle, if this has exactly the same temperature as the pole faces. If the poles are cooler, the point in question is displaced toward the cooler end, if they are the warmer, toward the warmer end, of the strip.

For each temperature stage in the measurement of  $Q$  or  $S$  a careful study should be made of such a temperature-gradient curve. Data for plotting it are obtained by measuring the temperature differences of points (1) and (2), (2) and (3), (3) and (4), (4) and (5), (6) and (7), (7) and (8), (8) and (9), (9) and (10), of Fig. 6, in the order given and then in the reverse order, first with the gradient running from right to left,

<sup>4</sup> Unwin, Proc. Roy. Soc. of Edin. 34, p. 210 (1913-14).

then with it running in the reverse direction. The gradient along the (1) to (5) line is not exactly the same as that along the (6) to (10) line, the edge of the strip being rather more affected by the inflow and outflow of heat than the median lengthwise line. Assuming that the gradient along the upper edge is the same as that along the lower edge, and so letting the lower-edge observations represent both edges, I have taken the mean of the (1) to (5) and the (6) to (10) observations, thus making the median line of equal importance with the two edges in estimating the general temperature-gradient. In palladium the temperature-gradient near the mid-length of the plate was usually about 10 percent less along the lower edge than along the median line, and, accordingly, taking the mean of these values was equivalent to reducing the first estimate of this gradient (made from the observed temperature differences between points (2) and (4) on the median line) about 5 percent. *This correction will be called correction (d).*

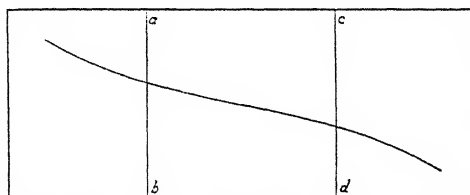


Fig. 10. The curve illustrates the variation of longitudinal temperature gradient along the experimental strip, in observations of the Ettingshausen and the Righi-Leduc effects.

Moreover, I have averaged the right-to-left gradient observations with the left-to-right gradient observations, making due allowance for inaccuracies of placing of the contact points. Thus I have obtained data for plotting a representative hot-to-cold curve corresponding to each mid-point temperature at which I undertook to measure  $Q$  and  $S$ . For example, I have plotted three such curves in the case of palladium, for the three mid-point temperatures  $25^\circ$ ,  $44.5^\circ$  and  $65^\circ$ , approximately. In fact, I plotted two such curves with a mid-point temperature near  $45^\circ$ , one with a mid-section temperature-gradient of about  $10.5^\circ$  per cm, the other with a gradient about half as great. For the first of these I used in one of the blocks  $B$  (Fig. 5) a stream of water at about  $11^\circ\text{C}$ . and in the other a stream of steam. For the second I used two water streams, one near  $30^\circ$  and the other near  $75^\circ$ .

All these curves were carefully plotted and carefully studied. The temperature corresponding to the point of inflexion of any curve I took to be the temperature of the pole-faces. It was usually a little below that

of the mid-point of the plate. Taking any given section of the curve, I could from the difference of gradient at the ends of this section estimate the amount of heat that leaked out from or into the corresponding section of the plate  $m$ . Then, knowing the mean distance from the plate to the pole-faces and, approximately, the mean difference of temperature between these faces and the section of the plate, I could make a rough determination of  $k$ , the thermal conductivity of the packing between the poles and the plate. Of course, slight inaccuracies in drawing the temperature-gradient curve might affect seriously the value found for  $k$  at any one section, but the errors of different sections tended to neutralize each other. Values found for  $k$  in the case of palladium, with a packing consisting mainly of cotton flannel, with one thin layer of mica, are given below:

TABLE II  
*Thermal conductivity of packing around the palladium strip*

Middle temp.	Middle gradient	$k$ below mid-point	$k$ above mid-point	Means
25°C	4.3°/cm	0.00021 0.00016 0.00019		
44.5	10.7	0.00028 0.00018 0.00014	0.00014 0.00026 0.00020	0.00019
45.5	5.5	0.00035 0.00021 0.00012		0.00020
65.1	5.5	0.00019 0.00015 0.00008	0.00028 0.00017 0.00010	0.00023
			Final mean	0.00016 0.00020

Kaye and Laby give 0.00023 as the thermal conductivity of flannel. It appears probable, therefore, that the leakage of heat was maintained, for the most part, by simple conduction between plate and poles, and not by convection due to air-currents moving upward or downward past the plate. That is, one can make a helpful estimate, in advance, of what the leakage will be by assuming that it will be caused by conduction only through the packing.

It is to be observed that, in my experiments on the Nernst and on the Righi-Leduc effect, I measure the difference of temperature of the two points (2) and (4) of Fig. 6, which are 2 cm apart, and assume, provisionally, that a uniform temperature gradient extends from one to the other, thus finding a value for the gradient at the mid-point. Careful study of the temperature gradient curves shows, however, that the mid-point

gradient arrived at in this way—that is, by taking the mean gradient between points (2) and (4)—is somewhat too large, perhaps 5 or 10 percent greater than the true value. Should we, then, make correction to the full extent of this divergence? This raises the question whether the effective longitudinal temperature-gradient, the gradient value which appears as  $\Delta$  in the formulas  $Q = \delta_e/H\Delta$  and  $S = \delta_h/H\Delta$ , for the Nernst and the Righi-Leduc coefficients, respectively, should be the precise value which holds at the mid-line of the plate between the junction point (8) in Fig. 6 and the opposite point on the upper edge of the plate. The discussion already given of “short-circuiting” due to parts of the plate or its connections in which the potential or temperature gradient is not the same as at the middle, requires us to answer this question in the negative. The proper value of  $\Delta$  to be used in the formulas above given is to be arrived at by a synthetic process in which the middle-half centimeter length of the plate will have a predominating but not an exclusive influence.

I shall assume that if we start at the middle cross-line of the plate and extend the length under consideration by 0.5 cm stages, the boundaries moving to right and left equally, each successive half cm length will affect the transverse gradient (of potential in the Nernst effect, of temperature in the Righi-Leduc effect) to an extent proportional to the product of the mean temperature-gradient (longitudinal) of this half cm by a *weight-factor* indicated by the significant figures set opposite this half cm length in the last column of Table I. I shall call the value of  $\Delta$  found in this way the *synthetic* value, or  $\Delta_s$ , and this is the value to be used in the formulas for  $Q$  and  $S$ .

The relations of  $\Delta_s$  to various gradients taken from the four temperature curves for palladium,  $\Delta_{0.5}$  for the middle 0.5 cm,  $\Delta_1$  for the middle 1 cm, etc., are shown in Table III.

TABLE III

*Longitudinal temperature gradients at different distances from the median line*

$\Delta_{0.5}$	$\Delta_1$	$\Delta_{1.5}$	$\Delta_2$	$\Delta_s$
4.04	4.14	4.17	4.31	4.26
9.24	9.74	10.16	10.76	10.07
4.88	5.00	5.21	5.52	5.25
4.76	4.94	5.18	5.48	5.17

It appears from this table that, on the average,  $\Delta_s$  was about 8 percent greater than  $\Delta_{0.5}$ , 4 percent greater than  $\Delta_1$ , 0.5 percent greater than  $\Delta_{1.5}$ , and 4.5 percent less than  $\Delta_2$ . Accordingly, the values first found for  $Q$  and  $S$ , in the case of palladium, were to be increased about 4.5 percent to make allowance for the too great value of  $\Delta$  provisionally used. *This will be called correction (e).*

*Transverse temperature-gradient; correction (f).* The method of measuring the difference of temperature actually existing at any time between point (8), of Fig. 6, and the opposite point on the upper edge of the plate, will be explained later. My view of the matter is that the Ettingshausen effect or the Righi-Leduc effect is all the time tending to increase the transverse temperature difference and that the heat conductivity of the plate  $m$ , assisted by the conductivity of the packing lying between the plate and the pole-faces, tends to reduce it. What we measure is the compromise result of these tendencies. We are now concerned with the question how much greater this difference would be if, other things being equal, the packing were thoroughly non-conductive for heat.

Study of the longitudinal temperature curve helps us here. For simplicity let us assume, for the present, that the temperature of the mid-point of the plate  $m$  is the same as that of the pole-faces, this bringing the point of symmetry of the temperature-curve to lie on the median transverse line of the plate, as in Fig. 10. Then the slope of the curve, at the line  $ab$  of Fig. 10, 1 cm to the left of the middle line, will be the same as the slope at the line  $cd$ , 1 cm to the right of the middle. This implies, if we neglect the slight difference of thermal conductivity due to difference of temperature, that the amount of heat carried by the plate across line  $ab$  is the same as the amount carried by it across the line  $cd$ . Moreover, this amount of heat is equal to that which would be carried from  $ab$  to  $cd$  by the plate alone, if the *temperature-gradient* existing at  $ab$  and at  $cd$  existed all the way from one line to the other, and it is considerably greater than the amount that would flow with a uniform gradient descending from the *temperature* of  $ab$  to the *temperature* of  $cd$ . In fact, if  $\Delta T$  represents the temperature of  $ab$  minus the temperature of  $cd$ , and if  $\gamma$  represents the *temperature-gradient* at  $ab$  and  $cd$ , the ratio of the heat actually conveyed from  $ab$  to  $cd$ , by plate, packing, etc., to that which would be conveyed by the plate alone, with the existing temperatures at  $ab$  and  $cd$ , is  $2\gamma/\Delta T$ . In some instances I have found this ratio to be as great as 1.19.

Turning now to the *transverse* conveyance of heat, let us suppose the line  $ac$  to be warmer than the line  $bd$ , and that we have measured their difference of temperature and found it to be  $\delta T$ . Assuming the plate to be of standard width, 2 cm, we find line  $ac$  analogous to  $ab$  and  $bd$  to  $cd$ , and so we conclude that, if the packing were non-conductive, the transverse temperature difference, in order to carry as much heat transversely as is now carried by plate and packing together, would have to be approximately,  $\delta T \times (2\gamma/\Delta T)$ . Accordingly, we amend our observed transverse

temperature-difference by means of the correcting factor  $(2\gamma/\Delta T)$ . This correction will be called correction (f).

I have provisionally made the assumption, in constructing Fig. (10), that the mid-point of the plate has the same temperature as the pole-faces, so that the line  $ac$  will be as much above the temperature of the poles as the line  $bd$  will be below that temperature. If this condition is not exactly maintained, and usually it will not be, a slight divergence from it will not seriously affect the accuracy of the correction just described. For example, if the pole-faces are a degree or two colder than the transverse mid-line of the plate, we shall have superposed on the equal out-and-in flows of heat which I have assumed, a flow outward from all parts of this transverse line. Such a flow will affect the transverse *gradient* in the plate but little, though it is better to keep it as small as practicable—that is, the poles should be kept as nearly as may be at the temperature of the middle of the plate.

*Thickness and method of support of plate.* It is evident that, other things being equal, the disturbing influence of heat leakage through the packing will be less the greater the thickness and the heat conductivity of the plate. The nickel plate I have used is about 0.058 cm thick, the cobalt plate about 0.053 cm, the gold plate about 0.0124 cm, the palladium plate about 0.0105 cm. Very thin plates are objectionable, even for the Hall effect, as it is difficult to measure their effective thickness with accuracy, and they are liable to serious mechanical injury unless very securely supported. Of course, where temperature gradients play no part, there is no objection to fastening the metal with cement to a glass plate; but such a backing is not desirable, in general, where temperature differences are concerned. Accordingly, my practice, when all four effects are to be measured, is to support the metal plate merely by its attachments to the blocks  $BB$ , Figs. (5) and (6). In the case of cobalt, however, since this metal, so far as my acquaintance with it goes, is very brittle, I felt obliged to use a backing of glass, which made the heat leakage greater than it would have been with a packing of flannel only.

In order to prevent buckling of the cobalt plate on heating, one of the leads  $B$  (see Fig. 6) was left slightly loose under its retaining screws, alignment being maintained by means of the guide  $G$ .

*Measurement of magnetic field strength.* Fundamentally, my method of measuring the field strength is to withdraw suddenly from between the pole-pieces a test-coil of known integral area, in circuit with a standard induction and a ballistic d'Arsonval galvanometer. But use of the test-coil is hardly practicable when a plate with all its small-wire attachments is in place between the poles. Accordingly I use the test-coil in



advance of the final installation of the plate, making observations of the galvanometer throw with various strengths of magnetizing current, and so getting data for plotting a curve showing the relation between the strength of this current and the intensity of the field. Two or three such curves should be made, each for a different temperature of the magnet pole-pieces, according to the range of temperature to be used in the main experiments.

When a magnetic metal plate is to be studied, it or an equally thick piece of like material should be in place between the poles when these observations with the test-coil are made.

Of course care should be taken to see that the distance between the pole-pieces is the same during the main experiments as during the preliminary test-coil work. I gauge this distance by means of a steel cylinder turned to the required thickness. Moreover, as the electro-magnet which I use suffers a perceptible decrease of pole-distance, unless care is taken to prevent it, when a strong magnetizing current is applied, I use a stop between the faces of the two magnetizing coils, near their upper edge.

#### MEASUREMENT OF THE HALL EFFECT

This operation is simple and easy, after the plate is properly mounted and connected. I have used a non-astatic Dubois-Rubens "armored" galvanometer of about 11 ohms series resistance, which rests on a platform suspended by three stout wires from a bracket bolted to a brick partition wall of the laboratory. Suspended beneath the platform is a vertical cylinder about 8 cm in diameter, which is partly submerged in an oil bath, to dampen vibrations. On the upper surface of the platform is a sheet of hair-felt about 3.5 cm thick, on which is a board about 2 cm thick carrying four rubber "sponges" compressed to a thickness of about 1 cm by the load they carry, which is a sheet of slate about 1.3 cm thick on which rest three glass cups receiving the feet of the galvanometer. I mention all these details because this Julius suspension arrangement, for which I am indebted to my former colleague Dr. E. R. Schaeffer, has proved eminently satisfactory, in a building subject to much disturbance, and has saved me a vast amount of work and worry.

The galvanometer, as I have used it, is not very sensitive. With a scale distance of 1.8 meters, 1 cm deflection is given by about  $1.8 \times 10^{-8}$  ampere. My ordinary method of determining its sensitivity is to find by trial how great a fraction of one volt is required to produce 1 cm deflection under the conditions of the actual Hall effect observations—that is, with



a greater or less amount of "introduced" resistance in the galvanometer circuit.

The galvanometer needle, provided with an air vane, has a vibration period of about 20 seconds, and is nearly "dead-heat." Readings with a reversal of the magnetic field at the plate  $m$ , are taken 45 seconds apart, a considerable interval being needed for all conditions to reach a final state after the reversal. As it is usually impracticable to arrange the side connecting wires at the plate in such a way as to make that part of the galvanometer circuit non-inductive, this circuit is opened just before the magnet reversal and closed a second or two after this reversal, a procedure which saves the needle from a too disturbing impulse.

It sometimes happens, especially at forced temperatures, that an appreciable longitudinal temperature-gradient exists at the middle of the plate during the Hall effect observations, thus superposing a Nernst effect. To eliminate error from this cause, two sets of observations should always be made, one with the longitudinal current running from left to right and one with its direction reversed. Another reason for this reversal is that it tends to exclude error that might otherwise come through a slight leakage of electric current from the magnet circuit into the galvanometer circuit. If reasonable precautions are taken, such leakage is not likely to be troublesome when the laboratory is artificially heated, but during the damp summer months it may become apparent and bothersome.

The temperature of the mid-part of the plate  $m$  during Hall effect observations can be found by means of a thermo-electric couple consisting of one of the junctions, let us say the top one, soldered to the plate (see Fig. 6) and another junction kept at a known temperature outside the magnetic field. The condition of this second junction is indicated in Fig. 11, which shows, one third full size, a double-walled glass tube, through the outer compartment of which runs water of the desired temperature while the inner contains oil of a sort that will not act injuriously on the wires that are immersed in it. An "ideal" wire  $I$ , leading from the junction on the plate, enters a narrow glass tube held in a cork stopper and extending nearly to the bottom of the oil. Near the bottom of this tube the ideal wire is soldered to a copper wire  $C$ , which, together with the copper wire coming directly from the junction on the plate, leads off to the galvanometer. A thermometer  $T$ , with the middle of its bulb on a level with the junction in the oil, gives the temperature of this junction.

The value of the Hall effect coefficient  $R$  as found directly from the observations made, is subject to the three corrections, (a), (b), and (c),

already described. Corrections (a) and (c) should be applied first and then (b), the latter being taken as a certain percentage of the value obtained by applying the (a) and (c) corrections. As correction (c) depends on the size of the Ettingshausen effect, the value of  $P$ , or rather the transverse temperature-difference actually existing because of the Ettingshausen effect, must be found before that of  $R$  can be finally determined.

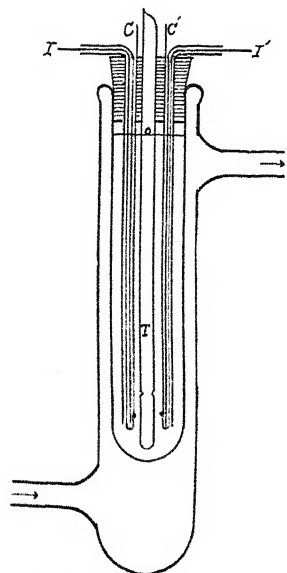


Fig. 11. Arrangement for controlling the temperature of thermo-electric couples.

The strength of the longitudinal current sent through the strip  $m$  should be adapted to the case in hand, the weakest current that will give satisfactorily large transverse effects being the best. Through a gold strip about 2 cm wide and 0.0125 cm thick, I used at times a current of about 30 amp.; but a current of equal strength sent through a palladium strip of like dimensions heats the middle many degrees, and is therefore objectionable unless a high temperature is desired.

Within the limits of accuracy of my observations, the transverse effect, whether of potential or of temperature, is, other things being equal, proportional to the strength of the longitudinal current. I do not, however, take this proportionality for granted in dealing with any new metal, and it is my custom to test it by experiment.

#### MEASUREMENT OF THE ETTINGSHAUSEN EFFECT

This effect consists of a small difference of temperature, sometimes not more than 0.01 degree in my experiments, between the same two points at which the attachments are made for measurement of the Hall effect. In fact, unless unusual precautions are taken to prevent the combination, these two effects always coexist. To measure the Ettingshausen effect alone, Unwin,<sup>5</sup> who has done good work on all four of the transverse effects, did not establish metallic contact of thermo-electric junctions with the two points in question, but used an interposed thin sheet of mica, making correction for the failure of this device to establish

<sup>5</sup> Unwin, Proc. Roy. Soc. Edin. 34, p. 208 (1913-14), and 41, p. 44 (1920-21).

complete equality of temperature between the junctions and the points on the plate at which they were applied. Thus he had only a single thermo-electric circuit and could connect this with an ordinary sensitive galvanometer in the ordinary way.

My method, much less simple in some aspects, has been to employ two independent thermo-electric couples, one having a junction soldered to one of the two points on the plate (see Fig. 8), the other having a junction soldered to the other of these points, and to connect these two couples to the coils of a galvanometer used differentially. The second junction of each couple is maintained at a known temperature, by being placed beside the other in an oil bath like that shown in Fig. 11.

My galvanometer, the same that I have used for measuring the Hall effect, was not intended for differential use, having only a single needle-group. To use it differentially for purposes of careful measurement was a somewhat novel and venturesome experiment, involving a rather complicated and laborious operation for determining the sensitiveness of the instrument as thus used. This operation ran as follows: With the two thermo-electric circuits sending their currents in opposite directions, one through coil *A*, the other through coil *B* of the galvanometer, the deflection produced by the introduction of a known e.m.f. into the circuit of coil *A* was measured, and next, with both the opposed currents reversed in the galvanometer coils, the effect of the same e.m.f. was measured again. Then corresponding measurements were made by introducing a known e.m.f. into the circuit of coil *B*. The variation of sensitiveness indicated by comparison of any two of these four measurements was often many percent, but the steadiness of the mean value of the four measurements through months of observation gave me great confidence in the substantial correctness of this mean. Nevertheless, I hope to use a properly wound differential galvanometer for measurement of the Ettingshausen and the Righi-Leduc effects hereafter.

Assuming it possible to keep the two oil-bath junctions (in Fig. 11) at the same temperature, one might suppose it to be a matter of indifference what this temperature was to be, but in practice it is found best to keep this temperature as nearly as may be the same as the mean temperature of the junctions on the plate *m*. If the difference between these two temperatures becomes large, there is so great an e.m.f. in each of the two opposing circuits that a slight change of resistance in one of them, such as may be due to local temperature influence, may upset their equilibrium enough to produce very troublesome galvanometer deflections. It is true that a compensating e.m.f. from a storage cell may be

introduced into each circuit in such a way as to make the net e.m.f. in each nearly zero, and of this device I make habitual use; but even so it is best to have the temperature difference in question as small as practicable; for storage cells are not always sufficiently constant in their e.m.f. to be depended on for much "compensating" action.

The two junction-points near the bottom of the oil-bath should be brought nearer together than they are shown to be in Fig. 11, due care being taken to prevent conductive contact of the two circuits, and these junctions should be symmetrically placed, so that, if possible, neither will be affected before the other by any change of temperature of the water stream surrounding the oil bath. Moreover, all thin wires in either circuit, and especially all junctions of thin wires, should be covered in such a way as to protect them from sudden temperature changes, such as a varying current of air or changing illumination might produce. Attention to such details may save a great deal of time and worry in the galvanometer measurements.

After the transverse temperature difference existing between the two side junctions on the plate *m* has been found by experiment, correction (a) should be applied, and to the value thus found corrections (b) and (f) should be added.

#### THE NERNST EFFECT

This effect, a transverse potential-difference accompanying a longitudinal temperature-gradient across the magnetic field, is not usually difficult to discover or even to measure. The longitudinal temperature-gradient, however, is naturally less convenient to deal with than a longitudinal electric current. I have said about all that I need say in regard to this matter, in my discussion of corrections (d) and (e). I do not, as a rule, have much trouble with inconstancy of this temperature-gradient, though it should be measured frequently.

Within the limits of accuracy of my observations, the Nernst transverse potential-differences, other things being equal, are proportional to the steepness of this gradient.

To reach the final value of the coefficient *Q*, corrections (a), (d), (e), (c) and (b) should be applied. The application of correction (c) requires knowledge of the transverse temperature difference, due to the Righi-Leduc effect, which accompanies the Nernst effect.

#### THE RIGHI-LEDUC EFFECT

This effect, a transverse temperature-difference accompanying a longitudinal temperature-gradient, across the magnetic field, is perhaps

even more troublesome to measure than the Ettingshausen effect, but I have already discussed most of the difficulties likely to be encountered here.

Within the limits of accuracy of my observations, the transverse temperature difference is, other things being equal, proportional to the longitudinal temperature gradient. The corrections to be applied are (a), (d), (e), (f), and (b).

#### QUALITY OF METALS; NUMERICAL RESULTS

The four metals that I have studied especially during the past two years are gold, palladium, nickel and cobalt.

The gold is the purest and softest obtainable from the S. S. White Dental Manufacturing Company of Boston.

The palladium is the purest that could be furnished me in February 1922, by Baker and Company of Newark. It was "of special high purity but not guaranteed chemically pure."

The nickel plate was given me by Leeds and Northrup and probably is of a high degree of purity, though its chemical analysis has not been made.

The cobalt was given me in 1913 by Dr. H. T. Kalmus of the Research Laboratory of the School of Mining, Kingston, Ont. He wrote "our cobalt runs very erratically from substantially pure metal to metal with nearly 1 percent of impurities." The plate probably contains some iron and nickel; as I have already indicated, it is decidedly brittle.

A summary table of the results obtained with these metals was given in the Proceedings of the National Academy of Science for July 1925, but as the values there given for  $P$  in palladium are all about 7 percent too large, the whole table, with the necessary correction, is here repeated.

TABLE IV  
*Values of R, P, Q and S in certain metals*

Metal	Temp.	$R \times 10^6$	$P \times 10^9$	Temp.	$Q \times 10^6$	$S \times 10^9$
Gold	17°	- 705	- 1.2	25°	- 181	-300
	72	- 696	- 0.4	57	- 181	-263
Palladium	26	- 845	+ 16.2	25	+ 327	- 48.7
	45	- 855	+ 17.8	45	+ 326	- 41.4
	64	- 844	+ 20.6	67	+ 335	- 37.8
Nickel	22	-4520	+ 60.6	38	+2590	-528
	57	-5910	+105.7	57	+3040	-494
	86	-7280	+154.2	77	+3660	-447
Cobalt	19	+3550	+ 81.0	25	+1900	+377
	48	+4440	+109.0	47	+2190	+429

A more detailed statement for one of the metals, palladium, may be of interest here, as it will give some idea of the precision of the measurements, their agreement or disagreement among themselves, and of the range of experimental conditions. In the following table,  $T$  indicates the tempera-

TABLE V

*Sample results for palladium*

These were obtained on various dates in Nov. and Dec. 1924 and in Jan. 1915 as indicated in parentheses; (N4)=Nov. 4 etc.

$T$	$I$	$R \times 10^6$	$P \times 10^9$	$T$	$G$	$Q \times 10^5$	$S \times 10^9$
28.0°C	414	-852(N4)		21.5°C	4.2	+327(D9)	
24.0	571	-836(D1)		24.7	4.4	+328(D23)	
28.0	410		+16.1(N4)	26.2	3.8	+326(J31)	
25.0	567		+16.5(D4)	24.5	4.2		-46.5(D10)
43.6	399	-862(N6)		26.1	4.4		-50.8(D22)
44.0	976	-846(D1)		45.8	10.9	+329(D30)	
47.0	633		+17.6(N28)	45.1	5.5	+322(J9)	
45.0	962		+18.2(N29)	45.4	10.6		-412(J2)
64.0	952	-844(N26)		45.2	5.6		-414(J7)
63.0	957		+20.3(N24)	67.0	5.5	+336(J13)	
64.0	943		+21.1(N26)	68.0	5.3	+332(J28)	
				66.0	5.4		-38.3(J15)
				66.8	5.0		-37.5(J30)

ture at mid-point of the plate under examination,  $I$  is the current density in amperes per square centimeter of cross-section of the plate,  $G$  is the longitudinal temperature-gradient. The intensity of the magnetic field varied from about 8700 to about 9200.

JEFFERSON PHYSICAL LABORATORY,  
HARVARD UNIVERSITY.  
August 12, 1925.

## A SMALL RESISTANCE THERMOMETER

BY GEO. F. TAYLOR

## ABSTRACT

**Small resistance thermometer.**—This thermometer, which was developed for field observations in the Department of Agriculture, fits into a sheath only about 6.4 cm long and 0.24 cm in diameter (and may be made even smaller). It consists of a Pb filament 1.5 cm long and  $2 \times 10^{-3}$  mm in diam. in a glass tube  $4 \times 10^{-5}$  mm thick, embedded in a typemetal which makes contact with one end of the filament. The method of drawing such filaments has been previously described.<sup>1</sup> The resistance of the filament is 448 ohms so that with a portable galvanometer a sensitivity of .005° is readily obtained. The temperature lag is about 10 sec. The technique of manufacture is described. After being made, the resistance decreases about .06 percent in the first two hours, then gradually increases about .05 percent, reaching a constant value in about 3 weeks. This time effect is due chiefly to the typemetal. After seasoning, the reading at 0°C is constant to within .02°. Fifty of these thermometers have been in service for some time, in the range -20° to 40°C.

**Thermal expansion of typemetal** (Pb 85, Sb 12, Sn 3).—The coefficient was found to be .864 times that of Pb, 0° to 100°C, or  $25.23 \times 10^{-6}$  per degree. After casting, rods were observed to decrease in length .06 percent, reaching a minimum, in 4 hr, .08 percent less than the initial length.

IN a recent number of the Physical Review mention was made<sup>1</sup> of a new type of small resistance thermometer. In the present article a detailed description is given of the construction of this instrument and of its performance.

The main object sought was to produce a resistance thermometer which would be comparable in size to the thermocouple and thus combine the advantages of both.

After considerable experimenting it was found necessary to make a radical departure from the ordinary coil-of-wire type, mainly for the reasons that for very small thermometers, the required sensitivity could not be obtained with the maximum current allowable and because no means could be found for supporting the wire in such a way that the resistance would remain constant. Thermometers were made by depositing films of metal on nonconductors but were not successful. Films of Pt, Au, Ag and Bi deposited on glass, quartz, mica, and calcite changed in resistance from  $\frac{1}{2}$  to 5 percent over a period of one month, and the heating was also too great.

The type of conducting unit which was finally found to be successful was a fine thread of metal drawn in glass and embedded in another metal.

<sup>1</sup> Geo. F. Taylor, Phys. Rev. 23, 658 (May, 1924).



## DESCRIPTION OF THE THERMOMETER

The external appearance of one of the set of fifty direct reading thermometers now in use (two-thirds actual size) is shown in Fig. 1(f), and an enlarged section in Fig. 1(e). The stem or case *A*, Fig. 1(e), which consists of a manganan or brass tube of .005 inch (.127 mm) wall thickness, 3/32 inch (.238 cm) diameter and 2.5 inch (6.35 cm) length, fits into a hard rubber head *h* of 3/8 inch diameter and 1/2 inch length. The head is provided with brass terminal posts, *P* and *P'* to which the connecting wires from the bridge (not shown) are attached with removable clips. The

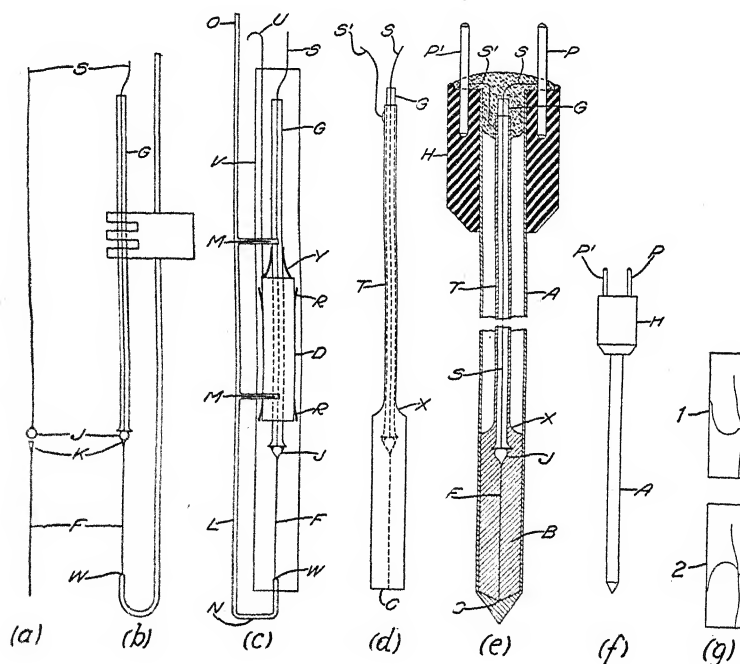


Fig. 1. (a)-(e). Details of construction of the thermometer.  
 (f) External appearance, two-thirds full size.  
 (g) Effect of meniscus on filament.

thermometers of this set were purposely made large and strong to stand rather rough usage though they may be—and in fact, some were—made only 1/32 inch in diameter and 2 inches long. This is as small as a 5 junction thermocouple of No. 40 wire can well be made and the depth of emersion necessary is no greater. The No. 33 copper or manganan lead wire *S*, which, when in the case, is soldered to the post *P*, fits in a glass tube *G*. On the lower end of the wire *S*, at the point *J*, a fine filament *F* is soldered. This filament, which will be referred to as the resistance element or unit,

is a Pb wire of about  $2 \times 10^{-3}$  mm diam., insulated with a covering of glass about  $4 \times 10^{-5}$  mm thick and has a resistance of 447.5 ohms. This filament *F*, including the lower ends of the leads *S* and *T*, is embedded in a mass of metal *B*, cylindrical in shape and 1 to 1.5 cm long, by flowing a fused alloy around these parts and allowing it to solidify. Type metal, having the composition 85 Pb, 12 Sb, and 3 Sn was the alloy used. The Pb filament *F* makes electric contact with the metal body *B* at the point *C*, and only at this point, since both the filament *F* and the lead *S* are insulated with glass throughout their length except at their soldered junction *J* which is insulated by a thin coating of porcelain cement. The return lead *T* is a copper or manganan tube of 1/32 in. diameter and .005 inch wall thickness which fits closely around the glass tube *G* and has its lower end embedded in or soldered to the body of metal *B* at the point *X*. When in the case, a short wire *S'* connects the upper end of the tube *T* to the terminal post *P'*. Manganan is preferable to copper because of its lower thermal conductivity, but both leads must, of course, be of the same material.

#### PERFORMANCE

The performance of the thermometer is well known only over the range  $-20^{\circ}\text{C}$  to  $40^{\circ}\text{C}$ . After a seasoning process, to be described presently, the ice point is constant within about  $0.02^{\circ}$ . The curve of resistance as a function of temperature over this range is straighter than that of free Pb. The probable reasons will be mentioned later.

When the thermometers are first made they undergo rather large changes in resistance and should be seasoned or aged for a period of two months or more before they are cut off to the desired resistance and finished. Immediately after casting, the resistance drops sharply (Fig. 2A), reaches a minimum value in about three hours and remains there for several hours, after which it rises gradually over a period of several weeks (Fig. 2B), then remaining constant within the limits already stated. Fig. 2A and B are characteristic curves which represent, without exception, the behavior of all of the large number observed. The total change of resistance during the period of seasoning may amount to as much as 0.06 percent of the total resistance.

Merk's "Blue Label" Pb was used and the temperature coefficient in all cases was  $.00401 \pm .00001$ .

Experiments were made to ascertain, if possible, whether the changes in resistance during seasoning were due to the alloy in which the filament was embedded, the glass surrounding the Pb filament, or to the Pb itself.

A rod  $a$ , Fig. 3, 48 cm long and 0.4 cm in diameter was cast from a specimen of the type metal used. This rod was seasoned by repeated boilings and allowed to rest at room temperature for four months. A similar rod  $a'$  was then cast and, as quickly as possible, the two were welded together at one end and placed in an upright position with the welded ends down. A yoke or rocker  $b$  bearing a small mirror  $c$  was placed across the upper ends. The two small rods of quartz  $r$  and  $r'$  rested separately on the two metal rods and carried, on their upper ends, two separate platforms  $i$  and  $i'$  for the points of support for the yoke bearing the mirror. The rods  $r$  and  $r'$  being of the same length and material and at the same

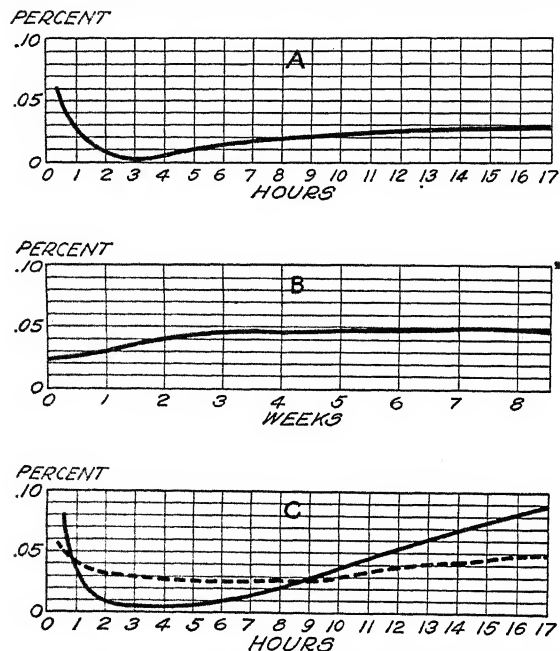


Fig. 2. A and B. Ageing effect on resistance of thermometer; percent change as a function of time.

C. Ageing effect on length of freshly cast rod of typemetal (full line curve) and of lead (dashed curve).

temperature, did not enter into the calculations. The points supporting the mirror were 0.502 cm apart and the mirror was observed through a telescope 4 meters away. This gave a multiplication of sixteen hundred times the motion between the two points of support and made it possible to detect a change in length as small as  $10^{-7}$  cm per cm. A glass jacket  $d$  around the two rods provided a means for a steam or ice bath.

The full line curve in Fig. 2C gives the results. The similarity of the curves shown in Figs. 2A and 2C indicates that most of the change in

resistance is due to type metal, doubtless through the pressure exerted upon the filament on shrinking and the release of pressure on expanding.

To ascertain whether or not Pb also undergoes a change of volume after fusing and resolidifying, a Pb rod which had been seasoned for several months was compared with a freshly cast Pb rod in the manner just described. The changes during the first ten hours are indicated by the dashed curve in Fig. 2C.

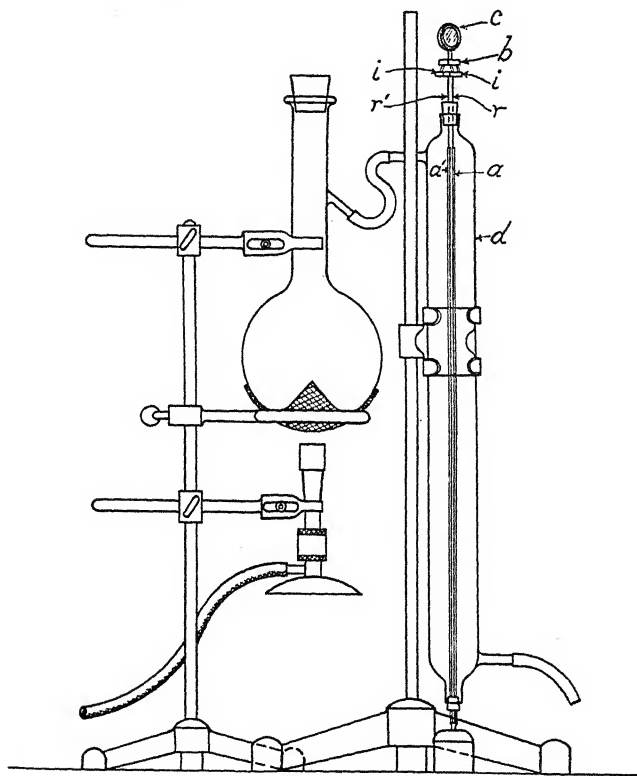


Fig. 3. Apparatus for studying the ageing effect on length of rods.

The coefficient of expansion of the type metal between 0 and 100°C was also determined by measuring the difference of expansion between two rods, one made of Pb and the other of type metal, in the same apparatus. Taking the coefficient of Pb as 29.30, that of the type metal was calculated and found to be  $25.23 \times 10^{-6}$ .

The Pb filament when embedded in the alloy, cannot expand more than the latter except within the narrow limits of the compressibility of the alloy and this only radially. The result is that, at the higher temperatures, the filament is under a greater pressure than at the lower temperatures

where it may even be under tension, and the temperature-resistance curve, which is normally steeper toward the higher temperatures, is straightened out by the resistance-pressure component which acts in the opposite direction.

The changes in resistance and probably also in volume, continue for indefinite periods after fusion, strong heating or distortion of shape, and it is not likely that they ever cease altogether in Pb or any other solid metal exposed to varying temperatures. It is not to be expected therefore that any newly made resistance thermometer will remain quite constant or that we can ever establish an absolute standard of temperature based on the resistance of a solid metal. The same may also be said of thermoelectric power.

It is well known that the electrical properties of metals cast in glass tubing are slightly different from those of the metals unconfined, but when the glass is made thin enough to behave as an elastic membrane and not as a rigid body ( $5 \times 10^{-5}$  mm or thinner) its effect upon the enclosed metal is negligible. Fibers of this degree of tenuity may be stretched a measurable percentage of their length or drawn red hot into water without breaking.

Since the temperature-resistance curve can be straightened by pressure, it does not seem desirable, in the case of Pb, that the thermal coefficient of expansion of the two metals be the same. But Pb was selected partly for its property of being self annealing at ordinary temperatures and it has not been determined whether or not the hard metals, under long continued pressure, would undergo strain hardening accompanied by a progressive increase in resistance. This effect, which is observed in a bent wire or coil, is the result of unsymmetrical strain, one side of the wire being under pressure and the other under tension, and is not well enough understood to enable us to predict the effect of uniform pressure upon a microscopic wire upon the resistance.

Recently quartz insulated filaments of Pt, Ir, Rh and some other very refractory metals have been made and it is quite likely that one of these embedded in a pure metal will have a more constant resistance than Pb in type metal, besides permitting a much higher temperature range.

*Heating and lag.* The heating is  $.01^{\circ}\text{C}$  for a current of 1.8 milliamp. By using a specially designed bridge with high resistance ratio arms<sup>2</sup> a sensibility of .01 ohm (or  $.01^{\circ}\text{F}$ ) was easily obtained with a portable galvanometer. The temperature lag is about 10 seconds.

<sup>2</sup> The writer is indebted to Dr. W. P. White of the Geophysical Lab., and to Dr. Frank Wenner of the Bureau of Standards, for this valuable suggestion.

## TECHNIQUE OF MANUFACTURE

A sample of Pb of the highest purity obtainable is melted and sucked up into glass tubes about 1.5 mm diam., the glass removed with HF and the remaining Pb rods cut into pieces about 1 cm long. A number of glass tubes, all slightly larger than those used for casting the rods, are next drawn. The walls of these tubes should be of such thinness that they can just be conveniently handled without collapsing between the fingers, which will be from 1/25 to 1/50 of the diameter. The glass recommended for this purpose is Corning G80.

Using the material already prepared, glass insulated Pb wire 2 or  $3 \times 10^{-3}$  mm in diameter is made by the process previously described<sup>1</sup> for use as the resistance element in the thermometer. Since one end of each resistance element must be soldered to a copper connecting wire, it is necessary that a short length of the larger wire from which it is drawn, be left attached (see *K*, Fig. 1(a)). The resistance of the filament may be measured at once by laying it across two Pb plates which are connected to a Wheatstone's bridge and cutting off the ends with a pen knife. The pressure of the knife edge welds the filament to the blocks at the points of cutting and completes the circuit through the filament.

The connecting wires just mentioned are made by cutting No. 33 bare or enameled wire into lengths of 3 or 4 inches, touching the end of each to an oxy-acetylene flame until it rolls up into a small globule, *J* in Fig. 1 (a), and tinning this end with soft solder. They are now ready to be soldered to the resistance elements, which is done as follows.

The resistance element, *F* in Fig. 1, already prepared is laid on a cork stopper with the enlarged end of the filament extending about 1 mm over the edge of the stopper and held in this position by a similar stopper placed upon it. The end of the filament is then moistened with soldering flux. The connecting wire *S* is clamped in a mechanical device by means of which it can be moved in any one of three directions. An adjustable microscope stage was used for this purpose. The wire should be clamped at a point about 4 cm from the soldered end. By this means the globular end *J* of the lead wire *S* is brought into a position such that the enlarged end *K* of the filament barely touches the center of the globule. One quick passage of a thin flame across the wire near the globule, but a safe distance from the filament, is all that is necessary to secure a good soldered connection. The wire *S* with attached filament *F* is then taken out of the clamp and a glass tube *G* 1/32 inch outside diameter is slipped over the wire until it is stopped by the globule *J*. The lead wire and attached filament then are placed in a temporary support (Fig. 1(b)) and the end of

the filament is attached at the point *W* to prevent it from becoming tangled or broken off. The soldered junction *JK*, Fig. 1(b) between the wire and filament is then covered with porcelain cement.

The filament or resistance unit is embedded by supporting it in the center of a tube and immersing this tube in a fused metal so that the metal, entering the end of the tube, flows around and encloses the filament, leaving when cooled, a solid cast with the filament embedded in its center. The filament is about the size of a spider's web and has no sensible rigidity and very little tensile strength. Unless it is supported near the center of the convex meniscus formed by the liquid metal in a glass tube, it is likely to be thrust aside and broken by the unbalanced surface forces of the liquid metal (see 2, Fig. 1(g)). If a concave surface is formed, as with a metal tube, the filament is held in the center without support (see 1, Fig. 1(g)). Glass was used, however, on account of its transparency.

The device for supporting the filament in the center of the tube is shown in Fig. 1(c). The upper support *D*, which is inside the casting tube *V*, is a short brass rod, provided with friction springs *R* to hold it in place and a hole through the axis for admitting the lead wire *S* with its insulating tube *G*. The lower support *L*, which is outside the tube, is a steel wire with one end attached to the tube by spring clips *M*, and the other end *N*, bent into a U shape which terminates along the axis of the casting tube *V*. Both supports *D* and *L* can be moved, either separately or together, along the casting tube by means of stiff wire handles *O* and *U* attached to the supports and extending past the upper end of the tube *V*. With the supports near the lower end of the tube *V*, the small tube *G*, carrying the filament and lead wire, is passed through the support *D*, and the end of the filament is attached with porcelain cement to the lower support at the point *W*. Both supports are then moved together to the position shown in Fig. 1(c). The casting tube (with all attachments) is now placed in a vertical position in the apparatus shown in Fig. 4, by which it can be moved up and down over a melting pot. The melting pot *P* is a solid copper cylinder with two holes *HH*, one for the metal from which the cast is to be made, and the other for a mercury thermometer.

Keeping the temperature of the melting pot always a few degrees above the melting point of the metal, the casting tube is slowly lowered into the fused metal until all the space below the upper support is filled. To prevent the metal from running back as the casting tube is raised, suction is applied with the mouth through the rubber tube *T* which is



slipped over the upper end of the casting tube. Care must be taken not to allow bubbles of gas from the cement to be trapped in the cast.

The cast is now slipped out of the tube and the supports removed. The return lead tube *T*, Fig. 1(d) and (e), is slipped over the glass tube *G*, and soldered to the head, or bulb, at the point *X*, Fig. 1(e). After this, it is put in a lathe and turned down to fit the case and the end cut off (also in the lathe) until the resistance is somewhat above the final resistance. After a period of seasoning an ice reading is again made and the

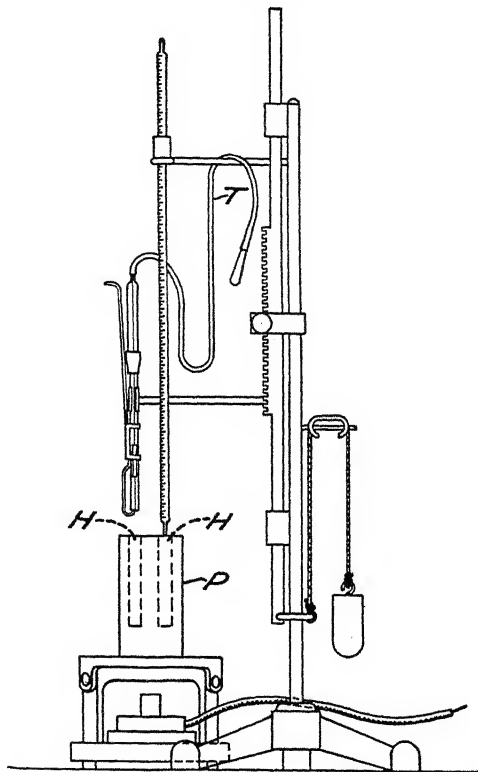


Fig. 4. Apparatus for casting typemetal around the filament.

thermometer is again put in the lathe and cut off just the amount necessary to bring it to the final resistance, after which it is plated with copper.

A precision jeweler's lathe with a slide rest and a special cutting tool were used. The thermometer, while turning in the lathe is connected to a bridge so that the resistance can be followed to a hundredth of an ohm at all times. The current is carried to and from the thermometer while in the lathe by rotating copper disks which dip in wells of mercury.

A lamp and scale were used with the galvanometer, and the scale, which was 2 m from the galvanometer, was placed just over the lathe so that the motion of the image could be followed without taking the eyes off the work. Although the filament is surrounded with glass, whenever the metal head in which the filament is embedded is cut through, a permanent contact is always made between the filament and the metal at the point of cutting.

After the upper ends of the lead wires  $SS'$ , Fig. 1(d) and (e), have been soldered to the terminal posts  $PP'$ , a mixture of equal parts of beeswax and rosin was melted and flowed over the top of the hard rubber head. This serves to support the lead wires  $S$  and  $S'$  and to prevent the formation of films of moisture between the terminal posts, should the thermometer be used in a damp place.

A feature to be noted about this type of thermometer is that large sets can be made equal to each other and of such resistance that 1 ohm is equivalent to  $1^{\circ}\text{C}$  or  $\text{F}$  so that they can be read directly on any bridge.

UNITED STATES DEPARTMENT OF AGRICULTURE,  
BUREAU OF PLANT INDUSTRY,  
WASHINGTON, D. C.  
March 4, 1925.

THE VAPOR PRESSURES OF METALS;  
A NEW EXPERIMENTAL METHODBY WORTH H. RODEBUSH AND ALFRED L. DIXON<sup>1</sup>

## ABSTRACT

**Quasi-static method of measuring vapor pressures.**—The vessel *A* containing the liquid and surrounded by a furnace for maintaining a uniform temperature, is connected by one tube *C* to a manometer *M* and a reservoir containing a neutral gas such as nitrogen at a suitable pressure, and by another tube *B* to an intermittent pump. Outside the furnace the two tubes are connected to opposite sides of a differential manometer *D*. Successive portions of the nitrogen are pumped off through *B* until the manometer *D* begins to show a permanent difference of pressure; then the reading of *M* is the vapor pressure desired. The action depends on the fact that when the pressure in *M* is less than the vapor pressure, nitrogen can get from *C* to *B* to equalize any difference of pressure caused by the pump, only by diffusion against the up-streaming vapor in *C*, and inter-diffusion in the case of a tube 3 to 4 mm in diameter is slow. A test of the method gave values for the *vapor pressure of mercury 170° to 203°C* only .04 mm greater on the average than those of Smith and Menzies.

**Vapor pressure of lead, 1118° to 1235°C** was found to vary from 5.70 mm to 19.70 mm in good agreement with the equation  $\log_{10} p(\text{mm}) = -10372/T - \log_{10} T - 11.35$ , which also fits the best results of Egerton at lower temperatures. The *heat of vaporization of lead at its melting point* is calculated to be 46,300 cal. The chemical constant comes out  $-1.40$  which is close to the value  $-1.59$  computed from the quantum theory of monatomic gases.

THE accurate determination of the vapor pressures of the less volatile metals is a matter of very considerable experimental difficulty. Because of the very high temperatures the exact measurement of the boiling point is out of the question, while the measurement of the boiling point under reduced pressure is subject to large errors because of radiation losses from the thermocouple and the tendency of vapors to superheat. The fact that these two effects cause errors in opposite directions does not reduce the uncertainty.<sup>2</sup> The dynamical method<sup>3</sup> has been applied at high temperatures but it seems to be very unsatisfactory. The best results are to be expected from some form of static method since we can attain a much more uniform and exact temperature in our apparatus if

<sup>1</sup> Research Fellow of the Chas. A. Coffin Foundation.

<sup>2</sup> The authors (Jour. Am. Chem. Soc. 47, 1036, 1925) have measured the vapor pressure of lead by this method. The mean of that series of observations is confirmed by our new measurements but the discrepancies between individual observations are very great.

<sup>3</sup> Haber and Zisch, Zeits. f. Physik 9, 325 (1922).

we minimize the rate at which heat is carried away from it. This is especially important since we have no liquids suitable for baths in a high temperature thermostat. In the ordinary application of the static method a portion of a vapor is trapped off over its own liquid in a U-tube, the liquid serving as a manometer. Such a method has been used successfully, for instance, in measuring the vapor pressure of mercury. At higher temperatures there are two serious difficulties: (1) The quartz glass or

other material becomes opaque so that we cannot read the level of the liquid, (2) because of the evolution of absorbed gases we cannot keep a pure vapor in the enclosed space. To avoid these difficulties the authors have evolved a method which approaches static conditions as a limit in operation.

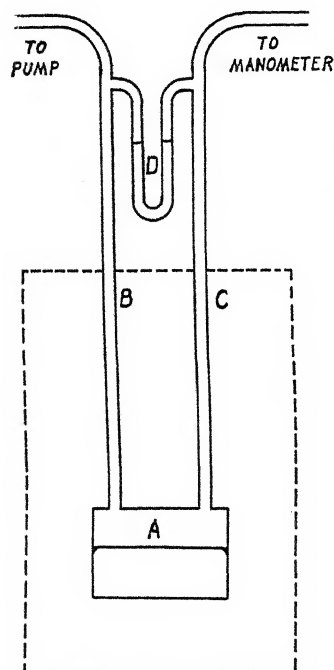


Fig. 1. Diagram of apparatus.

other material becomes opaque so that we cannot read the level of the liquid, (2) because of the evolution of absorbed gases we cannot keep a pure vapor in the enclosed space. To avoid these difficulties the authors have evolved a method which approaches static conditions as a limit in operation.

#### METHOD

The apparatus, constructed of Pyrex, quartz glass or other material suited to the working conditions, is shown diagrammatically in Fig. 1. The metal or other substance whose vapor pressure is to be obtained is contained in a shallow reservoir *A* not less than 2 cm internal diameter. The tubes *B* and *C* of 3 to 4 mm internal diameter are of sufficient length so that the upper part of the apparatus remains cool when immersed in a furnace to the depth shown by the dotted line. A differential manometer *D* is provided, containing a suitable liquid, such as paraffin oil. The temperature is measured by a thermocouple attached to the outer wall of *A*.

In operation the apparatus is filled with nitrogen to a pressure greater than the expected vapor pressure and the furnace is brought to constant temperature. Successive portions of nitrogen are pumped off through the tube *B*, sufficient time being allowed after each withdrawal for the liquid levels in the manometer *D* to stop moving. While the theory is somewhat involved the actual behavior of the apparatus is simple. So long as the pressure of the nitrogen in *C* is greater than the vapor pressure of the substance in *A* no permanent difference in level on the two sides

of the differential manometer can be established. As soon as the pressure of the nitrogen drops below the vapor pressure, the vapor in *A* acts as a valve to prevent the passage of nitrogen through from *C* to *B* and a permanent difference in level can be set up in the manometer *D*, which is approximately equal to the difference between the vapor pressure of the substance and the pressure of the nitrogen in *B*. For reasons which will be elaborated below it is necessary to obtain the reading when the difference is as small as can be observed in order to fix the vapor pressure with accuracy.

#### THEORY OF THE METHOD

While the apparatus works in a very simple manner it is not obvious why this is so, since diffusion effects might be expected to play an important part at higher temperatures. The theory which applies to the case has been elaborated by Gaede<sup>4</sup> and the reader is referred to his papers for the fundamental considerations. We have a vapor rising in a tube and being totally condensed against an external pressure of a gas. Let us call the partial pressure of the vapor *P* and the partial pressure of the inert gas *p*, using the subscript 1 to denote pressures in the reservoir *A* and the subscript 2 to denote pressures in the tubes *B, C* above the condensation line of the vapor. In the hydrodynamic equation for the flow of gases in tubes of 3 to 4 mm bore at 10 mm pressure, the term containing the viscosity of the gas is large in comparison with the term containing the coefficient of friction against the walls of the tube. If there were no gas above the vapor in the apparatus then the equation for the upward flow of the vapor (in gram mols per second) would be

$$m = \frac{\pi r^4 (P_1 + P_2)}{16 R T L \eta} (P_1 - P_2) . \quad (1)$$

Here *r* is the radius and *L* the length of the tube, *R* the gas constant, *η* is the coefficient of viscosity and *P*<sub>1</sub> and *P*<sub>2</sub> are the vapor pressures at the two ends of the tube. If now there is a gas with pressure *p*<sub>1</sub> above the vapor, then we have the added resistance of diffusion which may be treated as a pressure drop  $\Delta P = \Delta p$  equal in magnitude for gas and vapor but in opposite directions, Eq. (1) now becomes

$$m = \frac{\pi r^4 (P_1 + P_2)}{16 R T L \eta} (P_1 - P_2 - \Delta P) . \quad (2)$$

A similar equation holds for the gas. The vapor is being continually condensed in the upper part of the tube so that *P*<sub>2</sub> = 0. The gas is diffusing

<sup>4</sup> Gaede, Ann. der Physik **41**, 289 (1913); **46**, 357 (1915).

into the closed chamber *A* so that  $p_1$  must reach some limiting value and the gas flow become zero when the gas pressures on the two sides of the apparatus are equal.

Now if the gas flow is zero,

$$\Delta P = \Delta p = p_2 - p_1 \quad (3)$$

and Gaede obtains for the general conditions of equilibrium:

$$p_1 + P_1 = p_2 + \frac{16\eta D}{P_1 r^2} \log_e \left( \frac{p_2}{p_1} \right). \quad (4)$$

There are three cases to distinguish. For the case  $P_1 < p_2$  it is apparent that if any inequality in the pressure  $p_2$  is produced between the two sides of the apparatus, the gas must sweep through the vapor from one side of the apparatus to the other and equalize the pressure. It only remains to calculate the rate of reflux of the vapor up the tube since a too rapid escape of heat by this way would disturb the static condition desired. The equation for the rate of reflux is obtained by combining (2), (3) and (4), obtaining

$$m = \frac{\pi r^2 D}{RTL} \cdot \log_e \left( \frac{p_2}{p_1} \right). \quad (5)$$

Here *R*, the gas constant, should be expressed in c.g.s. units. So long as  $p_2 > P_1$  the term  $\log (p_2/p_1)$  must remain small and since the diffusion coefficient *D* is of the order of magnitude  $10^6$  at unit pressure, the rate of reflux will be very small indeed.

As the external pressure is lowered and we approach the condition  $p_2 = P_1$  we find that  $p_1$  at equilibrium is still appreciable and the term  $\log (p_2/p_1)$  may be calculated from Eq. (4). The coefficient of viscosity  $\eta$  has been shown to be of the order of magnitude  $10^{-3}$ . If we substitute rough values in c.g.s. units for the constants in (4), remembering that  $p_2 = P_1$ , we have

$$p_1 = \left[ \frac{2.3 \times 16 \times 10^{-3} \times 10^6}{1.3 \times 10^4 + (0.3)^2} \right] \log_{10} \left( \frac{p_2}{p_1} \right).$$

The numerical coefficient is approximately 30. Hence if  $p_2 = 10$  mm,  $p_1$  is less than 0.1 mm, and Eq. (5) shows that the rate of flow of the vapor up the tubes remains small.

If the external pressure is reduced considerably below the vapor pressure in *A*, then the rate of flow of vapor up the tubes will become so large that the vapor in *A* will (because of rapid escape of heat, etc.) become unsaturated; i.e. *P* will be less than the true vapor pressure

corresponding to the external temperature. This effect was always observed experimentally if the external pressure was lowered greatly. For this reason it is desirable that the reservoir *A* be of as large cross-section as possible. We can keep the unsaturation as small as we please by keeping the permanent difference of pressure which we set up small.

It remains to show that permanent difference of pressure can be maintained when the external pressure on one side is equal to the vapor pressure and on the other side is slightly less. Here it is a question of rate of diffusion. The equation for the rate of diffusion of the gas against the ascending vapor is given by the expression similar to Eq. (2).

$$m' = \frac{\pi r^4 (p_1 + p_2)}{16 R T L \eta} (p_2 - p_1 - \Delta P) \quad (6)$$

where  $\Delta P$  is the drop in pressure in the ascending vapor, which is to be ascribed to the "diffusion resistance." When  $p_2 - p_1 = \Delta P$  we have zero gas flow and the condition of equilibrium given by Eq. (2).

Now if  $p_2 = P_1$  on one side of the apparatus while  $p_2$  is decreased slightly on the other side,  $p_1$  will decrease and tend to remain in equilibrium with the lower value of  $p_2$ . For a first approximation let us assume that  $p_1$  is decreased by 1 dyne per  $\text{cm}^2$  but that the upward flow of vapor is undisturbed and hence unchanged in value. The net value of the last parenthesis in (6) will then be 1, and

$$m' = \frac{\pi \times (0.3)^4 \times 1.3 \times 10^4}{16 \times 8.3 \times 10^7 \times 10^3 \times 10 \times 10^{-3}} = 10^{-8} \text{ (approx.)}.$$

As a matter of fact the downward movement of gas against the ascending vapor means that  $\Delta P$ , the pressure drop in the vapor due to diffusion, must be increased, since the vapor flow is retarded and less of its pressure drop is expended on external friction. We have therefore used too large a value for the parenthesis in (6), and the rate of flow calculated is too great. In actual operation of the apparatus it was demonstrated repeatedly that a considerable difference of pressure could be maintained indefinitely between the two sides of the apparatus when the gas pressure was equal to the vapor pressure.

#### EXPERIMENTAL PROCEDURE

The difference in levels in the paraffin oil in *D* was read to 0.01 mm with a cathetometer. *C* was connected to one limb of a U-tube manometer, the other limb being connected to a pump capable of producing a high vacuum. Sulfuric acid was used as a liquid in this manometer and the difference in levels was likewise read with the cathetometer.



Sulfuric acid was used instead of mercury because of its smaller density and smaller surface tension. Not only is the absolute difference of level for a given pressure much greater but the percentage error from the capillary effects of dissimilarities in the sides of the manometer is greatly reduced.

Considerable experimentation was required to determine the exact size of the tubes *B* and *C* to give the most satisfactory operation. When *B* and *C* were too large, disturbing effects were produced by too rapid flow of the vapor up the tubes, while if they were too small they were clogged by the returning condensed liquid. A bore slightly in excess of 3 mm was found to be the most satisfactory.

#### VAPOR PRESSURE OF MERCURY

As a test of the method a number of determinations were made on mercury with a Pyrex apparatus. The apparatus was placed in an electrically heated oil bath and the temperatures were read with a copper-constantan thermocouple which had been calibrated at the boiling points of water and benzophenone. The results are shown in Table I together

TABLE I  
*Vapor pressure of mercury*

<i>T</i>	<i>P</i> (obs)	<i>P</i> (Smith and Menzies)
170.4°C	6.29 mm Hg	6.22 mm Hg
178.1	8.30	8.22
180.1	8.80	8.82
183.9	10.13	10.08
189.6	12.33	12.24
197.2	15.78	15.77
202.8	18.90	18.90

with values interpolated from the reliable measurements of Smith and Menzies.<sup>5</sup> The agreement is excellent. Any deviations are to be attributed to differences between the temperature scales used by Smith and Menzies and that of the authors.

#### VAPOR PRESSURE OF LEAD

In order to measure the vapor pressure of lead, the part of the apparatus which was to be heated was constructed of quartz glass. This part of the apparatus was placed in a Vitreosil test tube and this in turn inserted in an electric tube furnace mounted in a vertical position. The bulb *A* was placed about 10 cm from the bottom of the furnace and the lower part of the furnace was plugged with insulating material. The top of the furnace extended about 20 cm above the reservoir *A* and the

<sup>5</sup> Smith and Menzies, Jour. Am. Chem. Soc. 32, 1434 (1910).

vitreosil test tube was filled in around the tubes *B* and *C* with quartz beads. The furnace was wound with chromel wire. The temperature was measured by a Pt-PtRh thermocouple which was tied to the outside of *A* with platinum wire. The temperature was regulated with a hand controlled rheostat and it was not difficult to avoid fluctuations of more than 0.2-0.3 degree at 1200°C. Since the apparatus was insulated above and below and separated from the heating coil by double insulating walls it is believed that the temperature was not only constant but nearly uniform for a considerable distance above the reservoir. The thermocouple was calibrated at the melting points of potassium chloride<sup>6</sup> and potassium sulfate and showed only small deviations from the standard table of Adams.<sup>7</sup> The lead was free from appreciable amounts of impurities.

The results are shown in Table II. These results agree with the other measurements by the authors previously referred to but are in marked disagreement with those of Ingold<sup>8</sup> who also used the boiling point method. The only other data of importance on the vapor pressure of lead are those of Egerton<sup>9</sup> who used the method of Knudsen at much lower temperatures.

TABLE II

<i>T</i>	<i>Vapor pressure of lead</i>	
	<i>P</i> (obs)	<i>P</i> (calc)
1391°K	5.70 mm Hg	5.63 mm Hg
1408	6.80	6.83
1424	8.25	8.18
1441	9.86	9.85
1458	11.82	11.81
1475	14.21	14.10
1491	16.70	16.58
1508	19.70	19.66

When our data for  $\log p$  are plotted as a function of  $1/T$ , they lie on a straight line within very narrow limits. This would imply that  $C_p$  the atomic heat capacity at constant pressure was the same for molten lead as for lead vapor. The work of Iitaka<sup>10</sup> shows that  $C_p$  for liquid lead is apparently independent of temperature and equal to 7 calories. Since  $C_p$  for monatomic vapors is 5 calories, in setting up a vapor pressure equation we have assumed  $C_p = 2$  and have obtained the equation

$$\log_{10} P(\text{mm}) = 10372/T - \log_{10} T + 11.3500. \quad (10)$$

<sup>6</sup> Roberts, Phys. Rev. **23**, 286 (1924).

<sup>7</sup> Adams, "Pyrometry," Am. Inst. Min. Metallurg. Engineers, N. Y. (1920).

<sup>8</sup> Ingold, J. Chem. Soc. **121**, 2419 (1922).

<sup>9</sup> Egerton, Proc. Roy. Soc. **103**, 496 (1923).

<sup>10</sup> Iitaka, Science Reports, Tokohu Imp. Univ. p. 899 (1919).

The values calculated from this equation are shown in the third column of Table II. This equation also fits very closely those data which Egerton has designated as his best at lower temperatures. The heat of vaporization of lead at its melting point may be calculated by the Clapeyron relation from this equation; the value found is 46,300 cal.

In an apparatus of the sort described above, thermal effusion effects may be expected to produce errors. Careful experiments showed that with tubes of 3 to 4 mm bore the effects due to thermal transpiration were of the order of magnitude of 0.01 mm.

Since pressures can be read with a precision of 0.001 mm the accuracy obtainable with this method depends upon the temperature control and the patience of the operator. The exact location of the highest pressure at which a readable pressure difference can be maintained is necessarily a time-consuming operation.

#### THE CHEMICAL CONSTANT

According to the quantum theory of monatomic gases<sup>11</sup> the constant  $C_0$  in the following equation (in which  $M$  is the atomic weight)

$$\log_{10} p(\text{atm}) = -\frac{\Delta H}{2.3RT} + \frac{5}{2} \log_{10} T - \frac{1}{2.3R} \int_0^T \frac{C_p dT}{T} + \frac{2.5}{2.3} + \frac{3}{2} \log_{10} M + C_0 \quad (11)$$

should be equal to  $-1.588$ . Using the best values obtainable for specific heats and heats of fusion<sup>12</sup> to evaluate the integral and the values for  $\Delta H$  and  $\log p$  obtained from Eq. (11) above, we find<sup>13</sup>  $C_0 = -1.40$ . While it is difficult to estimate the experimental error, there is little doubt that it is sufficient to account for the discrepancy. The greatest source of uncertainty is probably in the specific heat values used both above and below the melting point.

LABORATORY OF PHYSICAL CHEMISTRY,  
UNIVERSITY OF ILLINOIS,  
May 6, 1925.

<sup>11</sup> Tetrode, *Ann. Physik* (4) **38**, 434 (1912).

Einstein, *Berl. Akad.* p. 261 (1924).

<sup>12</sup> The data for specific heats were taken from the work of Eucken and Schweser (*Verh. Deut. Physik. Ges.* **15**, 582, 1913), Griffiths and Griffiths (*Trans. Roy. Soc. London* **214A**, 319, 1914) and Iitaka, *loc. cit.*<sup>10</sup> The heat of fusion was also determined by Iitaka.

<sup>13</sup> Cf Simon, *Zeits. Physik. Chem.* **110**, 572 (1924). Simon uses the data of Ingold in his calculation and gets a value  $C_0 = -0.8$ . His theory that  $C_0$  is a function of the heat of vaporization appears to us to depend for experimental support upon Ingold's data.

## MERCURY VAPOR PRESSURE AT LOW TEMPERATURES

BY FRANKLIN E. POINDEXTER

## ABSTRACT

**Mercury vapor pressure, 20° to -80°C.**—A modified Buckley ionization gage is described with a range from  $10^{-2}$  to  $4 \times 10^{-9}$  mm. This was used to measure the vapor pressure of mercury. Correction for thermal effusion was made, ranging from 25 percent at -80°C to zero at 0°C. The gage was calibrated at 0°C from Knudsen's value. The results correspond to the equations  $\log_{10} p$  (liquid) =  $8.86 - 3.44(10^3/T)$ ;  $\log_{10} p$  (solid) =  $9.35 - 3.55(10^3/T)$ .

**Heat of vaporization of mercury, 20° to -80°.**—From a large-scale plot of  $\log p$  against  $1/T$  the heats of vaporization were calculated from the relation  $\lambda = -Rd(\log p)/d(1/T)$ . Above the melting point the results correspond to the equation  $\lambda = 15,900 - 10t$  where  $t$  is temperature centigrade. A slight discontinuity in slope of the  $(\log p, 1/T)$  curve gives at the melting point a sudden increase in the heat of vaporization of some 600 calories, which is in good agreement with the heat of fusion by direct experiment.

**A**SIDE from the theoretical considerations of thermodynamics, the use of mercury diffusion pumps, etc., in high vacuum work lends practical importance to a knowledge of the vapor pressure of mercury at different temperatures. The range from 0°C up has been covered by a number of representative experimenters such as Knudsen,<sup>1</sup> Smith and Menzies,<sup>2</sup> A. C. Egerton,<sup>3</sup> Menzies,<sup>4</sup> and others. Volmer and Estermann,<sup>5</sup> however, seem to have been the only ones to have covered the range from 0°C to -65°C. The present paper covers the range from 20°C to -80°C.

## EXPERIMENTAL METHOD

*Ionization pressure gage.* In the eighteen months of continuous work with the Buckley ionization gage preceding this research, the writer has constructed and used four different types of ionization gages and it seems not out of place to discuss here the details and advantages of the one used in the present research.

Dushman<sup>6</sup> points out the importance of keeping the various lead-in wires separated as far as is possible to prevent electrical leakage from one to the other over the glass. The writer finds that leakages may occur

<sup>1</sup> Knudsen, *Ann. der Phys.* **29**, 179 (1909).

<sup>2</sup> Smith and Menzies, *Jour. Amer. Chem. Soc.* **32**, 1434 (1910).

<sup>3</sup> A. C. Egerton, *Phil. Mag.* **33**, 33 (1917).

<sup>4</sup> Menzies, *Jour. Amer. Chem. Soc.* **41**, 1783 (1919).

<sup>5</sup> Volmer and Estermann, *Zeits. f. Physik.* **7**, 1 (1921). The writer wishes to thank Professor John Johnston of Yale University for calling his attention to this paper.

<sup>6</sup> Dushman, *Phys. Rev.* **17**, 7 (1921).

both inside and outside over the glass from one lead to another, so a system of nickel wire collars  $c_1$ ,  $c_2$ ,  $c_3$ , and  $c_4$  were incorporated in the structure. The protecting collars  $c_1$  and  $c_2$  are connected to ground. The collars  $c_3$  and  $c_4$  are maintained at  $-25$  volts, which is the same potential as that of the grid, by means of a separate wire leading directly to the battery. The filament  $F$  is a straight loop of 10 mil (.25 mm) tungsten wire braced by means of a tungsten wire thrust into the glass between the leads. The stem carrying the filament can be easily cut from the

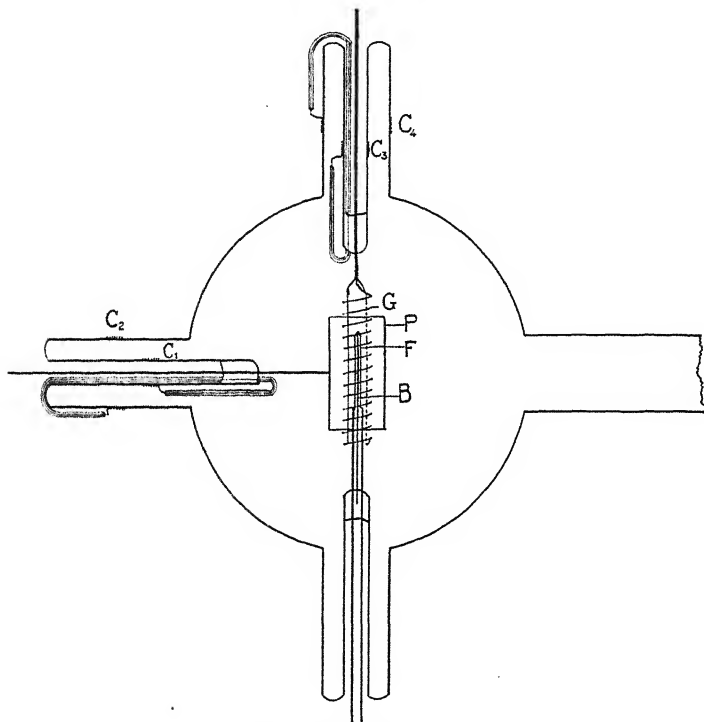


Fig. 1. Ionization gage.

gage and a new filament installed. The grid is a spiral of 7 mil tungsten wire carried by a 10 mil tungsten frame extending down each side, each end of the spiral being welded to the supporting frame. The plate  $P$  is of nickel and somewhat longer than the filament while the grid  $G$  is longer than the plate. This extra length in the plate and grid is a precaution against stray ions or electrons collecting upon the glass walls of the gage, which may give erratic results. The main part of the gage is a one liter Pyrex flask. It is made large so that its temperature while the gage is in use is considerably lower than the outgassing temperature.

The glass parts are of Pyrex glass and were outgassed by baking in the direct flame of a hand blow torch for an hour or so. The plate and grid were outgassed at a bright red heat by means of electron bombardment using a 10,000 volt transformer to supply the voltage between the filament and plate. When properly outgassed, the residual gas pressure is less than  $4 \times 10^{-9}$  mm, which is the limiting pressure that could be measured in this experiment.

The ionization gage is particularly well adapted for pressures below  $10^{-2}$  mm. Since it is an indirect method and the ionization for a given electron current is different for different gases, it is necessary to calibrate

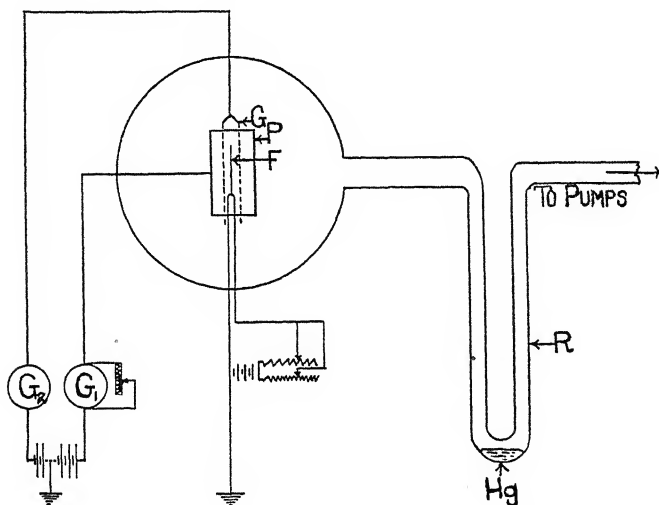


Fig. 2. Arrangement of apparatus.

the gage at some one temperature for mercury vapor. Then the ratio of the ionization in that gas at any other temperature to that at the calibrating temperature is equal to the ratio of the respective pressures.

The apparatus and the arrangement is practically the same as that used by the writer<sup>7</sup> in his work on the sodium trap for mercury vapor. The plate *P* Fig. 2, was maintained at +250 volts relative to the filament *F* by means of a storage battery. The galvanometer *G*<sub>1</sub> used to measure the electron current from filament to plate, was a Leeds and Northrup type P galvanometer having a sensitivity of  $2.7 \times 10^{-8}$  amp. per scale division. A universal shunt was used with *G*<sub>1</sub> which multiplied the electron current readings in steps of 10. The deflection of *G*<sub>1</sub> was held at

<sup>7</sup> Poindexter, J.O.S.A. and R.S.I. 9, 629 (1924).

100 mm throughout the experiment, the shunt being set at 10 to 1, 100 to 1, and 1000 to 1. This eliminated any possibility of error due to non-uniformity of the galvanometer scale. The grid *G* was maintained at -25 volts with respect to the filament. The positive ions formed by the collisions of electrons with the molecules of gas between *F* and *P* were collected on the grid *G*. The ion current from *G* was measured by the highly sensitive, critically damped, Leeds and Northrup type R galvanometer *G*<sub>2</sub>, having a sensitivity of  $8 \times 10^{-10}$  amp. per scale division. The sensitivity of this galvanometer was found to be constant over all parts of the scale.

The U shaped tube *R* was used as a mercury reservoir. The mercury used was twice distilled in a current of air according to the method described by Hulett.<sup>8</sup> Liquid air was first placed about the lower portion of the reservoir and the apparatus thoroughly outgassed. Then the liquid air was replaced with cooled alcohol, care being taken that the alcohol extended several inches higher than the part cooled by the liquid air. The temperature of the bath was raised in steps of some 7°C by adding small quantities of alcohol with stirring. The time between readings varied from over an hour at low temperatures to approximately 25 minutes at the highest. It takes some time for mercury vapor to reach equilibrium after the temperature is changed. This appears to be due to a "soaking in" process into the surface of the glass. A few minutes heating of the glass with liquid air on the reservoir is sufficient to drive off this surface mercury, but 24 hours are not sufficient without heating. For increasing temperatures, equilibrium is obtained in the times allowed between readings. For this reason, all of the runs had to be taken with increasing temperatures.

A platinum resistance thermometer of approximately 25 ohms resistance and carrying a current of .01 ampere was used to determine the temperatures. The potentiometer balance method against a standard held at constant temperature was used, the balance being obtained through a Leeds and Northrup type R galvanometer. The platinum thermometer was calibrated three times at the ice, steam, and liquid oxygen points, the first two calibrations being made before starting the experiment and the last one near the end. These calibrations checked. The constants and potential differences found by Callander<sup>9</sup> and others are in close agreement with those of this thermometer, so it is thought that the temperatures are probably correct to 1/100°.

<sup>8</sup> G. A. Hulett, Phys. Rev. 1st series 21, 388 (1905).

<sup>9</sup> Callander, Phil. Mag. 47, 191 (1899).



## RESULTS

The vapor pressure  $P'$  in the ionization gage  $G$  is proportional to the ratio of the positive ion current  $I$  to the electron current  $E$ . That is,

$$P' = K I/E$$

Knudsen's value of  $P'$  (.0001846 mm) at  $0^\circ\text{C}$  was used to calibrate the gage. When  $P'$  is in mm of mercury,  $I$  in scale divisions and  $E=1000$  scale divisions, then,

$$K = 3.91 \times 10^{-6} \text{ mm/1 scale division ion current.}$$

The results are given in Table I. After much preliminary work to ascertain the best working conditions, the runs labeled A and B in the table were made Jan. 28th and 29th respectively. The values of  $P'$  are given in column six of Table I as uncorrected pressures because the pressures above the mercury in the reservoir are not directly proportional to the positive ion current on account of the phenomenon of thermal effusion as pointed out by Knudsen,<sup>10</sup> West,<sup>11</sup> and others.

TABLE I

*Data for vapor pressure of mercury at low temperatures.*

Run	Temp.	Electron current $E$	Ion current		Vapor pressure	
			$I$	$kI/E$	$P'$ (uncorr.)	$P$ (corr.)
A	-79.61°C	$2.66 \times 10^{-3}$ amp.	.1	.001	$4.00 \times 10^{-9}$	$3.00 \times 10^{-9}$
B	-69.94		.2	.002	$8.00 \times 10^{-9}$	$6.00 \times 10^{-9}$
A	-66.89		.6	.006	$2.00 \times 10^{-8}$	$4.00 \times 10^{-8}$
B	-63.72		.4	.004	$1.56 \times 10^{-8}$	$1.27 \times 10^{-8}$
A	-57.76		1.5	.015	$5.87 \times 10^{-8}$	$4.85 \times 10^{-8}$
B	-56.88		1.6	.016	$6.26 \times 10^{-8}$	$5.18 \times 10^{-8}$
A	-49.89		7.2	.072	$2.80 \times 10^{-7}$	$2.37 \times 10^{-7}$
B	-43.43		21.9	.219	$8.56 \times 10^{-7}$	$7.31 \times 10^{-7}$
A	-42.80		22.8	.228	$8.92 \times 10^{-7}$	$7.52 \times 10^{-7}$
A	-41.79		25.5	.255	$9.98 \times 10^{-7}$	$8.54 \times 10^{-7}$
B	-37.84	$2.66 \times 10^{-4}$ amp.	40.7	.407	$1.59 \times 10^{-6}$	$1.38 \times 10^{-6}$
B	-32.74		79.7	.797	$3.12 \times 10^{-6}$	$2.72 \times 10^{-6}$
A	-30.97		108.3	1.083	$4.24 \times 10^{-6}$	$3.71 \times 10^{-6}$
B	-28.14		165.7	1.657	$6.48 \times 10^{-6}$	$5.70 \times 10^{-6}$
B	-22.74		335.7	3.357	$1.31 \times 10^{-5}$	$1.17 \times 10^{-5}$
A	-20.57		47.2	4.72	$1.84 \times 10^{-5}$	$1.752 \times 10^{-5}$
B	-17.22		65.8	6.58	$2.60 \times 10^{-5}$	$2.460 \times 10^{-5}$
A	-12.00		138.0	13.8	$5.40 \times 10^{-5}$	$5.213 \times 10^{-5}$
B	-10.81		155.9	15.59	$6.10 \times 10^{-5}$	$5.895 \times 10^{-5}$
A	- 5.71		263.0	26.3	$1.028 \times 10^{-4}$	$1.005 \times 10^{-4}$
B	- 3.98	$2.66 \times 10^{-5}$ amp.	323.5	32.35	$1.265 \times 10^{-4}$	$1.240 \times 10^{-4}$
A	+ 0.21		48.2	48.2	$1.885 \times 10^{-4}$	$1.887 \times 10^{-4}$
B	1.76		55.8	55.8	$2.181 \times 10^{-4}$	$2.190 \times 10^{-4}$
A	7.99		108.8	108.8	$4.260 \times 10^{-4}$	$4.320 \times 10^{-4}$
B	10.86		145.0	145.0	$5.670 \times 10^{-4}$	$5.786 \times 10^{-4}$
A	13.04		179.9	179.9	$7.038 \times 10^{-4}$	$7.206 \times 10^{-4}$
B	19.73		298.5	298.5	$1.165 \times 10^{-3}$	$1.210 \times 10^{-3}$

<sup>10</sup> M. Knudsen, Ann. d. Physik **31**, 205 and **33**, 1435 (1910).

<sup>11</sup> G. D. West, Proc. Phys. Soc. **31**, 278 (1919).

## THERMAL EFFUSION CORRECTION

A correction for thermal effusion between two regions of different temperature in a system is necessary when the mean free path is great compared to the dimensions of the parts connecting the two regions. In this research the tube connecting the Hg reservoir to the ionization gage was approximately 1 cm in diameter, and since the mean free path at the highest pressure measured ( $1.2 \times 10^{-3}$  mm) was of the order of 2 cm, it is necessary to make this correction. Fortunately this correction for thermal effusion is a comparatively simple matter. If the two regions are at the temperatures  $T_1$  and  $T_2$  degrees absolute then their respective pressures are related by the equation

$$P_1/P_2 = \sqrt{T_1/T_2}. \quad (1)$$

In this particular case, let us designate the temperatures and pressures in the two regions—the Hg reservoir and the ionization gage—as follows. Let  $P_{RT}$  and  $P_{RO}$  = pressures above Hg in the reservoir  $R$  at any temperature  $T$  and at  $0^\circ\text{C}$ , respectively. From Knudsen's work  $P_{RO}$  is assumed equal to .0001846 mm.

$P_{GT}$  and  $P_{GO}$  = pressures in ionization gage  $G$  when  $R$  is at temperatures  $T$  and  $0^\circ\text{C}$ , respectively.

$T$  = temperature absolute in the reservoir  $R$ .

$T_{GT}$  and  $T_{GO}$  = temperatures of ionization gage when  $R$  is at temperatures  $T$  and  $0^\circ\text{C}$ , respectively.

Then as in equation (1) we have,

$$P_{RT}/P_{GT} = \sqrt{T/T_{GT}} \text{ and } P_{RO}/P_{GO} = \sqrt{273/T_{GO}}.$$

Solving these equations for  $P_{RT}$  we have,

$$P_{RT} = P_{RO} \frac{P_{GT}}{P_{GO}} \sqrt{\frac{T}{273} \times \frac{T_{GO}}{T_{GT}}}. \quad (2)$$

Now  $P_{GO}/P_{GT} = S_0/S_T$  where  $S_0$  and  $S_T$  represent the scale deflections of ion current at temperatures  $273^\circ$  and  $T$  respectively. The temperature of the gage remains constant as long as the electron current is constant so that in this particular case  $T_{GO} = T_{GT}$  and equation (2) becomes simply

$$P_{RT} = .0001846 \frac{S_T}{S_0} \sqrt{\frac{T}{273}}. \quad (3)$$

When, however, the electron current is changed from that at which the gage was calibrated—1000 scale divisions in this case—then the

temperature of the gage changes by a small amount. We can get at the temperature of the place where ionization occurs as follows.

First, assuming Stefan's Law, and taking the area of the anode as 81 times that of the filament, we may estimate the temperature of the anode if the temperatures of the filament and of the bulb surrounding the anode are known, and this can be taken as sensibly equal to that of the gage.

There were three electron currents used as indicated in column 3 of Table I, namely  $2.66 \times 10^{-5}$ ,  $2.66 \times 10^{-4}$  and  $2.66 \times 10^{-3}$  amp. respectively. Since the area of the filament was  $1/4 \text{ cm}^2$  these currents are equivalent to  $1.064 \times 10^{-4}$ ,  $1.064 \times 10^{-3}$  and  $1.064 \times 10^{-2}$  amp. per  $\text{cm}^2$ . Substituting these values in Richardson's equation for thermionic emission we readily compute the corresponding temperatures of the filament  $T_f$  to be  $1825^\circ$ ,  $1900^\circ$  and  $2076^\circ\text{K}$ , respectively.

The temperature of the bulb was observed to be approximately  $325^\circ\text{K}$  when  $T_f$  is  $2076^\circ$  and  $300^\circ\text{K}$  when  $T_f$  is  $1825^\circ$ . These values of filament and bulb temperatures yield  $708^\circ$  and  $615^\circ\text{K}$  as the maximum and minimum temperatures of the gage. Therefore, the correction factor in the case of the largest current is  $\sqrt{T_{G0}/T_{GT}} = \sqrt{615/708} = .93$ ; for the medium current it is .987. It will be seen that the correction for temperature changes in the gage is small and hence our rough method of calculation may be taken as sufficiently accurate.

It will be noticed from column 4 in the table that the ion current readings for the first four points are less than 1 mm, and are therefore only approximate. In fact even the fifth and sixth points are liable to an error of some 12 percent since the scale could not be read closer than .2 mm.

The results of runs A and B are also represented in Fig. 3, curve *a*,  $\log p$  being plotted as a function of  $1/T$ . It will be noticed that the graph is almost a straight line, but that there is indication of a slight discontinuity in slope near the melting point. This discontinuity together with the slopes of the two parts will be discussed later on in the paper.

#### COMPARISON WITH OTHER RESULTS

The work of Volmer and Estermann<sup>5</sup> was referred to in the introduction. The dotted curve *b*, Fig. 3, is plotted from their values. It will be noticed that their values are slightly higher and that there is no indication of a break at the melting point. They, as well as the writer, used Knudsen's value of .0001846 mm at  $0^\circ\text{C}$  to calibrate their apparatus, so the two curves agree at  $0^\circ\text{C}$ . The agreement from  $0^\circ\text{C}$  to  $-40^\circ\text{C}$  is close con-

sidering that both methods are indirect and entirely different. The slight departure may perhaps be explained as follows. No mention is made in their paper of a temperature-gradient correction from bath to surface of mercury. Of course if this gradient were the same at the high and low temperatures, then it would cancel out in the calibration, but if this gradient is greater at  $0^{\circ}\text{C}$  than at  $-60^{\circ}\text{C}$  as a study of their apparatus

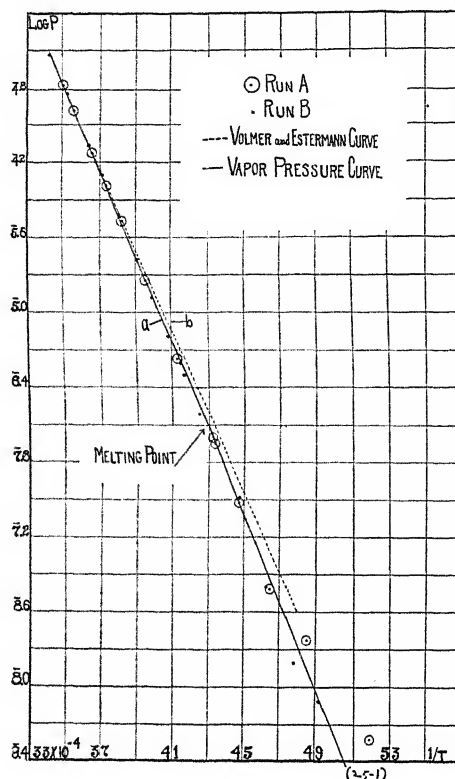


Fig. 3. Logarithm of pressure as a function of  $1/T$ . Curve a: Results of two runs indicated respectively by dots and by dots in circles. Curve b: Curve given by Volmer and Estermann.

indicates that it probably was, then the pressures at the lower temperatures would be progressively higher as the gradient diminishes. This would give a departure from the writers' curve in the same direction as that shown in Fig. 3.

#### THEORETICAL CONSIDERATIONS

From the fact that the heat of vaporization  $\lambda$  varies but little with the temperature, we may assume as a first approximation that the deviation

is a linear function of the temperature. Making this assumption we have,

$$\lambda = \lambda_0 - \alpha T, \quad (4)$$

where  $\lambda_0$  is the heat of vaporization at the absolute zero. Substituting for  $\lambda$  its value from the well known equation

$$\lambda = RT^2 d(\log p)/dT \quad (5)$$

and integrating, we get the equation,

$$\log p = -\frac{\lambda_0}{RT} - \frac{\alpha}{R} \log T + i \quad (6)$$

where  $i$  is the constant of integration. This is of the form

$$\log p = A - \frac{B}{T} + c \log T \quad (7)$$

which is the well known empirical vapor pressure equation. Now

$$\lambda = \frac{RT^2 d(\log p)}{dT} = -R \frac{d(\log p)}{d(1/T)}.$$

In Table II,  $\lambda$  is given in calories per gram molecule as calculated from the slope of a large scale  $\log p$  vs  $1/T$  curve similar to that of Fig. 3. If these values of  $\lambda$  are plotted as a function of  $T$ , two things are noticeable: (a) The graph is linear above the melting point; (b) there is a distinct\* discontinuity at the melting point. While it appears that the

TABLE II  
Heat of vaporization of mercury, computed from  
vapor pressure curve

Temperature		$\lambda$
289.21°K	16.11°C	15600
281.69	8.59	15800
273.97	0.87	15800
266.67	-6.43	16000
259.74	-13.36	16100
253.16	-19.94	16200
246.91	-26.19	16300
240.96	-32.14	16200
235.30	-37.80	16400
229.17	-43.93	17100
224.72	-48.38	17200
219.78	-53.32	17100
215.05	-57.05	17150
210.52	-62.58	17100
206.18	-66.92	17100
0	-273.1	(19900)

graph below the melting point is fairly straight, the points are too scattered to draw anything but very approximate conclusions both as

\* It should be borne in mind that the four lower points are of little value in determining the slope as the probable error is large.

to the heat of fusion and the slope. This scattering of points is due to the fact that the ion current at these low temperatures is near the limit of the galvanometer used. We may, however, as an approximation draw the best possible straight line through these points parallel to the graph of the points above the freezing point. This extrapolates to  $\lambda_0$  (solid) = 19,900 cal. The liquid curve gives  $\lambda_0$ (liquid) = 19,300 calories. Thus we have,  $\lambda_0$ (solid) -  $\lambda_0$ (liquid) = 600 calories as the heat of fusion, which is in fair agreement with the experimental value of 570 calories.<sup>12</sup>

So far as is known to the writer, no experimental values of the heat of vaporization of mercury have been determined within the range of this experiment. Folger and Rodebush,<sup>13</sup> however, found the heat of vaporization at 142°C to be 14,490 calories per gram molecule. The writer found the value from the mean heat curve to be 15,700 calories at 20°C and 16,300 at -39.5°C or an average decrease of 10 calories per degree rise in temperature (i.e. in Eq. (4)  $\alpha = 10$  cal./degree). Assuming their value is correct at 142°C, the mean temperature coefficient from 20° to 142° is 9.9 cal./degree, in practically perfect agreement. The value they calculated for 20°C (14,670 cal.) is, however, evidently too low.

The writer wishes to thank Professor A. Ll. Hughes for his untiring interest and helpful suggestions throughout this research.

WASHINGTON UNIVERSITY,  
ST. LOUIS, MISSOURI,  
February 13, 1925.<sup>14</sup>

<sup>12</sup> Phys. Chem. Tabellen (Landolt-Börnstein-Roth), 4th ed., p. 829 (1912).

<sup>13</sup> Folger and Rodebush, Jour. Am. Chem. Soc. 45, 2080 (1923).

<sup>14</sup> Received June 1, 1925—Ed.

## BOOK REVIEWS

**A System of Physical Chemistry. Vol. II. Thermodynamics,** W. C. M. Lewis. Issued as one of the textbooks of the Ramsay and Donnan series in Physical Chemistry. —This is the 4th edition revised and enlarged of a work that has already attained a very considerable circulation among physicists and chemists. While the greater part of the work is devoted to the application of thermodynamics to chemical equilibria, a discussion of the principles of thermodynamics is given in the first chapters.

Thermodynamics has always been a difficult subject for the student, probably because of the way in which it has usually been presented. The author follows the customary treatment but does very well with it, e.g. his presentation of the concept of entropy as a complete differential will probably be grasped by the average student as readily as any that can be given. He makes frequent use of the cycle in his derivations and many will approve this. It may be remarked, however, that the cycle is used to obtain a differential coefficient and when a mathematician wishes to differentiate he does not always go through the process of obtaining the increment of a function and passing to the limit, even in beginning calculus. The book appears to contain no discussion of absolute entropy or partial molal quantities. The chapters on activity and the Debye-Hückel theory of electrolytes should prove valuable. Many will feel that the concept of osmotic pressure has been given more space than it deserves.

The work is encyclopaedic in character, some of the chapters being little more than abstracts of original papers. A great many references to recent literature are given and the book should prove valuable to the advanced student of thermodynamics.—Pp. 489, Longmans Green and Co., New York, \$4.75.

W. H. RODEBUSH

**Ostwald-Luther, Physiko-Chemische Messungen, 4th Edition.** Edited by Carl Drucker.—The third edition appeared in 1909 and included 573 pages. The present edition has been enlarged through an extension of several sections and the addition of two chapters dealing, respectively, with x-ray analysis of solid substances and measurements relating to radio activity, making the total number of pages 814.

The earlier editions, after the first, were more or less outgrown at the time they came from the press. With the present edition an attempt has been made to bring the subject matter up to date. In this, the Editor has been only partially successful. An examination of the text shows that, with the exception of the newly added chapters, many of the methods described in detail are antiquated. In most instances literature references are given to more recent methods but a detailed description of these has usually been omitted and it is not, as a rule, possible for the reader to determine what method would prove the best suited to his purpose. A few examples may be given in illustration: The fifth chapter, comprising 36 pages is devoted to thermostats and thermostatic devices. Here we find illustrated the old thermostatic arrangement of Ostwald which at the present time is of historical interest only. Many of the devices and methods illustrated or described have long since been replaced by more refined ones. Chapter 6 is devoted chiefly to glass blowing. This section is inadequate in the present edition, as it was also in the earlier ones. It has little practical value either to the beginner or to the expert. Little is said regarding the properties of glass as a function of its composition, a matter which is of the greatest importance in both scientific and technical practice. A paragraph of four lines relates to the blowing of fused quartz and the one suggestion there made is misleading. Fused quartz is one of the most important laboratory materials of the present day and a knowledge of its properties is indispensable, while the technique of its manipulation is readily acquired. Four pages are devoted to methods for the purification



of water. The discussion indicates a lack of first hand knowledge of the modern technique of water purification. A very detailed description is given of the older forms of vacuum pumps while a description of mercury vapor pumps is omitted. Such pumps (of glass) may be constructed with ease and at a very low cost by the amateur as well as by the professional glass blower.

Too much space is devoted to older methods and far too little to newer and more refined ones which have superseded them. By elimination of the older material the necessary space could be obtained for an adequate discussion of contemporary practice. Those who have had considerable experience in the technique of physico-chemical measurements will find many valuable suggestions in this book, but it is not to be recommended to those who are not in a position to form their own judgment with regard to merits of different methods or appliances.—Pp. 814, 564 fig., 3 plates. Akademische Verlagsgesellschaft, Leipzig, 1925.

CHARLES A. KRAUS

**Stellar Atmospheres:** A Contribution to the Observational Study of High Temperature in the Reversing Layers of Stars. CECILIA H. PAYNE. (Volume I of Harvard Observatory Monographs: Harlow Shapley, Editor).—It is seldom that a "thesis fulfilling the requirements for the degree of Doctor of Philosophy" requires such extended notice. This book, of about two hundred pages, is a valuable accession to the permanent literature of astrophysics; it discusses in a very readable fashion the interpretation, in the light of recent physical theory, of the stellar spectra obtained at Harvard.

The student of stellar atmospheres seeks to deduce from the spectrum of a star the physical conditions at its surface—in particular the temperature and density. The problem is complicated by the fact that the outer regions of a star are neither completely transparent nor completely opaque; some light reaches the spectroscopist from depths of hundreds of kilometers, and both temperature and density increase downward. The laws of black-body radiation, the theory of gas-opacity, the Saha-Fowler theory of temperature-ionization, with the Fowler-Milne extension to the occurrence of maximum abundance of atoms of a given sort (as temperature and density vary)—these constitute the theoretical tools employed in this phase of astrophysics.

*Stellar Atmospheres* touches on each of these, and adds a valuable bibliography of the whole subject; consequently the book is worthy of a place in every physical, as in every astronomical, library. Chief place is given to observational material, including a detailed discussion, element by element, of lines in stellar spectra, and intensity-measurements, through the Harvard sequence, of lines of known series relations. The latter comprise a great amount of hitherto unpublished material. (These measurements are on an arbitrary scale; the problem of absolute measurements of line-intensity in stellar spectra remains to be solved.) The following are among the conclusions worked out: The surface temperature of the hottest stars is as high as  $35,000^{\circ}\text{K}$ ; previous estimates of very low densities for stellar atmospheres ( $10^{-4}$  atmospheric, or less) are well confirmed; the relative abundance of elements in stellar atmospheres is indicated as roughly the same as in the earth's crust—a fact of much importance for the student of atomic nuclei.

This book is the more deserving of attention because it is the first of a new type of publication from the Harvard Observatory.—Pp. x+216, 10 fig., 1 plate, Harvard Observatory, 1925. \$2.50.

JOHN Q. STEWART

**An Introduction to Fluid Motion.** W. N. BOND.—Professedly "a guide to one embarking on the study of fluid motion," this little book of 80 text pages presents manifold facts and formulas usually found in books on hydraulics and the motion of gases. It is a short cut to results rather than a systematic exposition. Euler's equations,

the stream function and velocity function are ignored, though vastly important in hydrodynamics.

Chapter I treats of steady flow in stream tubes and free jets, presenting the usual hydraulic equations and describing simple devices for determining velocity and pressure. Flow through an orifice is treated dimensionally, furnishing a first glimpse of the dimensional theory of fluid motion developed later.

Chapter II expands this theory and applies it to motion through tubes as well as orifices. Half this chapter is devoted to manometers and devices for determining the speed or form of flow through tubes.

Chapter III gives 10 pages to the motion of surface waves of a liquid; 4 to motion in channels and over weirs. The first is an elementary and interesting treatment of a large subject.

Chapter IV, in 12 pages, presents the important subject "motion of a body through a fluid." The treatment is unnecessarily qualitative, since we have useful quantitative expressions for the velocity and pressure about many geometrical forms, and for the resistance of spheres, cylinders, discs, etc. It furnishes interesting speculation on the generation and effect of eddies behind such bodies.

Chapter V, in 10 pages, discusses the effect of compressibility on fluid motion. It develops formulas for sound waves, the flow of gas through nozzles and orifices, the conservation of energy in gaseous flow.

The text has a pleasing number of footnotes citing important references, especially references to recent English writings on fluid motion. The citation of foreign sources, however, is too meager for a balanced educational work.—Pp. 94, 38 fig., Longmans, Green and Co., 1925. \$1.65.  
A. F. ZAHM

**Mechanics and Heat.** WILLIAM BALLANTYNE ANDERSON.—This is a revised and enlarged second edition of a well written elementary text suitable for a high school or first year college course. The selection and arrangement of topics is along conventional lines. The presentation is clear, and many of the difficulties arising in the mind of the student which the ordinary text slides over without comment are discussed and explained. The author's denomination of kinetic reaction as a "resisting force" seems, however, rather unfortunate; for the average student has difficulty in thinking of a resisting force as anything other than a resistance proportional to some function of the velocity.—Pp. xiii+371, McGraw-Hill, 1925. \$2.50.  
LEIGH PAGE

**A Treatise on Electricity, Second Edition.** F. B. PIDDUCK.—This is an excellent text of intermediate grade on the subject of electromagnetism. In addition to the usual treatment of the subjects of magnetostatics, electrostatics, and electric currents, the author has included fairly extensive chapters on Electricity in Gases, Röntgen Rays, Radioactivity, and the Electrical Theory of Matter, which are thoroughly up to date as regards the subject matter which they include. The last chapter, for instance, carries the Bohr theory through the theory of the Stark effect and the relativity theory of the fine structure of line spectra.

The book is prefaced by a mathematical introduction which has to do mainly with the important theorems of vector analysis which are needed in subsequent chapters. To one who has been brought up on the suggestive notation of Gibbs the author's notation seems very artificial and awkward.

The printing is worthy of the high standard of excellence maintained by the Cambridge University Press. Table of contents and index are both provided.—Pp. xiv+664, Cambridge University Press, 1925.  
LEIGH PAGE

**Electricity and Magnetism.** R. G. SHACKEL.—This is an excellent text for a high school course in electricity and magnetism. The subject is introduced by a consideration

of the properties of magnets, static electricity coming next, and current electricity last. The author is to be commended for developing the electron idea at the very start of the section on electrostatics, and explaining static charges and currents in terms of this conception. Only the most elementary mathematics is made use of—nothing more than the elements of algebra and geometry, and very little of these. The author discusses the concept of force and its measurement in an early chapter, so the book is suitable for a student who has had no previous acquaintance with the subject of physics.—Pp. vi +250, Longmans, Green and Co., London, 1925. \$1.20.

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